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Illinois State Water Survey Division

ATMOSPHERIC CHEMISTRY SECTION

SWS Contract Report 468

STUDY OF ATMOSPHERIC POLLUTION SCAVENGING

Twenty-Third Progress Report
Grant Number DE - FG02 - 88ER60635

August 1989

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Sponsored by:
United States Department of Energy
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THE REMOVAL OF ATMOSPHERIC SO_2 BY DRY DEPOSITED ROAD DUST

Allen L. Williams

Introduction

It is well established that dry deposition is a major process in the removal of atmospheric sulfur dioxide (SO_2), and that the dry deposition velocity of SO_2 is significantly influenced by the chemical properties of the receiving surface[1]. The influence of surface properties on the deposition velocity can characterized by the surface resistance defined in the resistance model[2] as one of the component resistances that compose the total resistance, itself defined as the reciprocal of the deposition velocity. Under environmental conditions two factors that are considered important for determining the SO_2 surface resistance are the extent of vegetative covering and surface wetness. The stomata on plant leaves are significant sinks of SO_2 but they close at nighttime causing a large diurnal variation in the surface resistance and, consequently, the deposition velocity. Surface wetness reduces the surface resistance, and is a significant factor especially during the winter months. The general picture for SO_2 dry deposition that has emerged is that over a wet surface the surface resistance is so low that the total resistance, and hence the deposition velocity, is controlled by the rate of turbulent transfer. Over vegetative surfaces the deposition is controlled by a combination of aerodynamic and surface effects while the stomata are active, but with the closing of the stomata at nighttime and during plant dormancy the deposition is limited by the high surface resistance.

The question raised here deals with the effect on SO_2 deposition of alkaline dust, especially $CaCO_3$, which is emitted by vehicular traffic on unpaved roads and settles across the landscape. The scenario presented is that large amounts of alkaline material is emitted and, due to its low emission heights and large particle sizes, deposits within a few kilometers of the source. Despite the limited transport distances, it is estimated that the deposited dust covers about half of the landscape, nationally, as a consequence of the large extent of unpaved roads. The purposed hypothesis is that SO_2 dry deposition surface resistance is significantly decreased by the road dust material, with the effect of increasing the amount of SO_2 dry deposition, especially to plant surfaces while the stomata are inactive, and enhancing the effect of surface wetness on SO_2 deposition.

Dust Deposition

The experience of driving behind another vehicle on an unpaved road during dry conditions provides strong evidence that unpaved roads are a large source of aerosol particles. The Atmospheric Chemistry Section of the Illinois State Water Survey (ISWS) under contract with NOAA has conducted a research effort to determine the effect of dust emissions from unpaved roads on acid rain neutralization. During the coarse of this work measurements of the amount of dust emitted from particular roads at varying vehicle speeds were made[3] in order to obtain a suitable parameterization of the emission factor[4,5] (the mass of aerosol emitted per distance of vehicular travel). A computer model was constructed[6] to estimate the amount of dust and alkaline elements emitted nationally based on our emission factor parameterization and Department of Transportation (DOT) estimates of the milage and daily use of unpaved roads. These modeling efforts show the total calcium emission from dust particles less than 10 microns in diameter to be in the neighborhood of 10 million tons/year[7,8]. When compared to the other main dust sources of soil erosion, dust devils, and agricultural tillage[9], the unpaved roads are estimated to represent 40.3% of the total mass while accounting for 68.8% of the calcium emitted to the atmosphere.

Some of the dust emitted, even if only that below 10 μm diameter is considered, dry deposits in the neighborhood of the road. Plume depletion studies, in which the particle flux is measured at the source and at some distance downwind, generally predict rather severe particulate depletion. Sehmel[10] reported plume depletion measurements for surface releases in which both a non-depositing tracer and submicron particles, which exhibit a minimum dry deposition velocity, were released simultaneously and measured at different distances downwind. The results reported were 37-44% plume depletion across a 1.2 km fetch of sagebrush and, in another case, 44 to 74% plume depletion across a 1.2 to 1.7 km evergreen forested fetch. Only a few

percent depletion would be expected from calculation. Other reported results of plume depletion from surface releases are 97% plume depletion over 3.2 km", 65% depletion between 45 and 91 m[12] and 80% depletion at 200 m[13,14]. Doran and Horst[15] reported downwind concentrations of depositing and non-depositing tracers. The depositing tracer (ZnS) with mean mass diameter slightly less than ten μm, was found to have a deposition velocity of from 1.1 to 4.21 cm/sec in the flat desert grass and sagebrush terrain. The high deposition velocities were associated with high wind speeds and a plot of the ratio of the ground concentrations of the depositing to the non-depositing species versus distance downwind was fairly consistent for each of the six experiments reported. It was found that about half of the depositing tracer had been dry deposited at 1 km downwind. It seems plausible, based on these plume depletion studies and road dust size distribution information (our measurements showing very little of the mass being below 2.5µm), that the road dust aerosol plume largely dry deposits locally within a few kilometers of the road.

One important consideration for judging the significance of SO_2 scavenging by road dust is the amount of land area that becomes covered by significant dust accumulations. Assume the dust for each km of travel all settles out in an area of 1 km^2 on each side of the road. The product of this with the total length of gravel roads for a given state gives the area over which significant dust accumulation occurs. Reckoned as a percent of the total state area, and averaged over the 48 contiguous states, the coverage is 52 percent This calculation discounts the fact that some areas may actually receive dust coverage from more than one road. On the other hand, the dust probably travels more than 1 km from the road. It, therefore, appears that about 50 percent of the landscape is subject to dry deposition of dust from unpaved roads. Since the length of graveled roads has remained relatively constant over the past sixty years[16], with the graveling of unimproved roads approximately keeping pace with the hard-surfacing of existing graveled roads, the dust covering of a significant portion of the total landscape appears to be a lasting feature of the environment.

The view advocated, then, is that dust generated from vehicular traffic on unpaved roads covers about half of the total landscape, even though it dry deposits locally. Further, the amount of calcium in the dust is approximately equal to the anthropogenic SO_2 emissions on a charge equivalent basis; if all the road dust calcium carbonate would react to form calcium sulfate by the adsorption of SO_2, it would account for slightly less than the anthropogenic SO_2 emission of 20 millions tons/year. Since the material is deposited on the landscape in the form of small particles with a large surface to volume ratio, it presents a large effective surface for the deposition of SO_2. The individual particles would be in a position to scavenge SO_2 for a period of several days until they are removed by natural processes or become saturated by SO_2 adsorption. Further, the dust covering of the landscape is a continual process during dry conditions, so the scavenging surfaces would be gradually replaced by fresh surfaces thus continually renewing the effect

Sulfur Dioxide Deposition

The SO_2 deposition velocity is often defined in terms of its reciprocal, the total resistance r_t In a simplified approach r_t can be taken as the sum of the component resistances

$$r_t=r_a+r_d+r_s \qquad (1)$$

Here r_a is the aerodynamic resistance depending on the turbulent transfer in the air above the surface, r_d is another fluid transport resistance attributed to molecular diffusion just above the adsorbing surface, and r_s is taken as the surface resistance which refers to the ability of the surface to adsorb the depositing species. As shown by Hicks and Matt[17], the diffusive resistance, r_d, for SO_2, as contrasted with that of aerosols for example, is small enough not to be the controlling resistance. Neglecting r_d, typical daytime values of r, and r_s for SO_2 deposition over a grass surface in the summer[18] are 3 and 1 sec/cm respectively, yielding a deposition velocity of .8 cm/sec. In this case the turbulent transfer is fairly efficient, and the total transfer is limited by the stomatal uptake of the grass. Corresponding nighttime values are r_a=1 sec/cm and r_s=5 sec/cm, yielding a deposition velocity of .2 cm/sec. The aerodynamic resistance increase reflects the usual calmer wind conditions at night, while the increase in surface resistance reflects the well known effect of the stomata closing at night. It is interesting that, when the process of SO, adsorption is modeled by including land use statistics that reflect regionally distinct deposition resistances , a spacial average over the Eastern U.S. clearly reflects the diurnal variation in deposition velocity which in a springtime scenario studied ranges

between .8 and .2 cm/sec The model also predicts that the SO_2 deposition increases over a wet landscape, it no longer being limited by the surface resistance, and the diurnal variation smoothes out. If the road dust SO_2 deposition sink turns out as strong as suggested here, the effect would be much like a continually wet landscape.

The notion that deposited dust is a good sink of SO_2 is supported by the efficient uptake of SO_2 by soil. Garland et al.[20] using the micrometeorological gradient method, measured the SO_2 deposition velocity over bare calcareous soil of 1.2 cm/sec. Since the soil was sufficiently rough to give an aerodynamic resistance of order 1 sec/cm, the calcareous soil appeared to act as a perfect sink of SO_2 This example and others discussed in a review by Chamberlain[1] (1980) point to bare soil as a good sink of SO_2, especially when the soil contains moisture and is alkaline. Judeikis and Stewart[21] reported laboratory measurements of SO_2 deposition to different cement mixtures of from 1.6 to 2 cm/sec under conditions where the atmospheric transport does not limit the deposition. They found that the capacity of the material to adsorb SO_2 increased with relative humidity. Their measured adsorption capacities for moist cement compared favorably with those reported by Braun and Wilson[22] for limestone. Judeikis and Stewart[31] also estimated that under these conditions a fresh limestone or moist cement surface would be saturated to SO_2 deposition in 11 days in the absence of some process like precipitation that would rejuvenate the surface activity for SO_2 removal. The issue of monument degradation due the dry deposition of SO_2 is identical to the process identified here for the SO_2 deposition to road dust. In the monument case the accumulation of gypsum, as the resulting salt from the reaction of sulfate and limestone, results in a increase of the surface resistance[23] that would not be as strong a factor in the road dust case due to the continuing deposition of dust on the canopy. It is interesting that in the interpretation of data from a St Louis monument experiment[24], it is hypothesized that dust depositing on the monument adsorbs the depositing SO_2 thus protecting the structure.

Alkaline aerosol material has also been shown to be a good sink for SO_2 adsorption and conversion to sulfate. According to Butler[25] analysis of deposited CaCO, particles from .3 to 10 *fita* in diameter showed that, of the 30 percent by mass which were high in calcium, about half was as $CaCO_3$ and the rest $CaSO_4$. An experiment was performed showing that up to 20 percent of the $CaCO_3$ particulate mass deposited on a test surface converts to $CaSO_4$ per day when exposed to the atmosphere. The work of Liberti et al.[26] distinguished between the physical adsorption of SO_2 onto various atmospheric particulate samples, and the conversion to SO_4. Of the 14 atmospheric and industrial emission samples studied, all materials adsorbed SO_2 in a laboratory setting with the amount adsorbed increasing with increased humidity. It was found that the alkalinity of the dust is a determining factor in favor of the conversion to SO_4, since adsorbed SO_2 could be driven off upon heating of acid particulates. The magnitude of the bond energies, measured by differential thermal analysis, indicated physical adsorption of the SO_2 to the particulate surfaces. However, the alkaline samples, including particles collected at a cement factory stack, would not desorb SO_2 upon heating and the sulfur was additionally determined to be present as SO_4 from x-ray photo-electron spectroscopy. $CaCO_3$ appears to be a strong sink for SO_2, and appears to efficiently convert the SO_2 to sulfate preventing re-emission to the atmosphere.

An argument based on the crude assumption that a deposited dust particle has the same ability to scavenge SO_2 as an open plant stomata provides an independent way to judge the potential magnitude of the effect According to our measurements of the mass distribution of dust emitted from various unpaved roads, the shape of the mass distribution is fairly constant Our unpublished measurements show the mass contained between incremental logarithmic diameters, dm/dln(D), is proportional to D_{35}, where D is particle diameter and m is particle mass. Assuming all particles are between 1 and 10 μm diameter, dm/dln(D) can be integrated to yield a total particulate mass. Equating the particulate mass to the emission factor, which is the mass emitted per km by a single vehicle, the constant of proportionality can be evaluated. Then assuming spherical particles, the number of particles emitted per km per vehicle can be estimated. If the particles are deposited on an area of 1 km^2 for each km traveled, the canopy area is assumed to be 5 times the ground area, and the emission factor is taken as 1.4 kg/veh-km, then approximately 1000 particles/cm^2 can be expected on the leaves for each vehicle pass. For comparison there are about 10^4 stomata/cm^2 on plant surfaces. In a slightly more sophisticated approach, using our model estimates for the emission factor and the DOT estimates of the number of graveled roads with their corresponding traffic volume estimates, it is found that after 4.14 days the number of deposited particles equals the number of plant stomata over a distance of 1 km on each side of the road. If a particle is capable of SO_2 adsorption for something like 11

days as estimated for cement and limestone bulk surfaces, it appears that the continual addition of fresh dust to the canopy would prevent the deposited particles losing their SO_2 reactivity due to prolonged exposure.

The dust particles can be viewed as providing a parallel resistance to the leaf stomata. Under the assumptions that the dust particles are each as efficient as an open stomata and that there are equal numbers of stomata and dust particles, the canopy resistance of the dust would equal the daytime stomatal resistance. Taking the stomatal and dust resistances as parallel and following to the example quoted at the beginning of this section, the total daytime canopy resistance would decrease from 1 to .5 sec/cm. With the same value for the aerodynamic resistance of 3 sec/cm, the deposition velocity would increase from .8 to 1.25 cm/sec during the day. At night the stomatal resistance would still increase to 5 sec/cm while the dust resistance is assumed to remain constant at 1 sec/cm, making the total canopy resistance equal to .8 sec/cm. Assuming the same nighttime aerodynamic resistance of 1 sec/cm, the total resistance becomes 1.8 sec/cm. This yields a nighttime deposition velocity of .6 cm/sec compared to .2 cm/sec without dust Assuming eight hours of darkness in this summertime example, the average deposition velocity increases from .6 cm/sec to 13 cm/sec due to postulated SO_2 uptake of dust

Dry-Bucket Data

Additional support for the supposition that deposited dust is a sink for SO_2 can be found from the National Acid Deposition Program/National Trends Network (NADP/NTN) dry-bucket data. If dry-bucket data for the eastern contiguous United States[27] (31 states between Minnesota and Louisiana and eastward) is considered, the amount of Ca and SO_4 show a high degree of correlation (see Figure 1). When each is expressed in terms of charge equivalents, they are found to be present in equal amounts as shown by the one-to-one line drawn through the data. This indicates that all of the calcium depositing in the buckets is converted to $CaSO_4$. The relation does not apply in the western states where an excess of Ca is found in the buckets. These measurements are consistent with the notion that the Ca containing road dust particles deposit and adsorb SO_2 to form $CaSO_4$. The dry bucket data is collected over 8-week periods, so deposited particles could be exposed to atmospheric SO_2 for a period of several weeks. In contrast, aerosol measurements do not show such a correlation, since the aerosol sulfate is known to be largely NH_4SO_4.

Concerns that have been expressed*[29], to the effect that the dry buckets tend to over-sample and collect more large particles then other surrogate surface arrangements, do not alter the conclusions drawn from figure 1, but support the idea that whatever amount of calcium is deposited an equal amount of sulfate eventually appears. It has further been shown that various degrees of screening of the data do not alter either the calcium or sulfate concentrations in the dry buckets[27], so the correlation is not likely associated with a contamination problem. Periodic high moisture or humidity in the buckets is a possibility for contributing to SO_2 scavenging since, for example, some moisture can get into the dry-bucket at the beginning of a rain before the wetness sensor is activated to cover the dry-side bucket, but by their design the dry-buckets are intended to prevent moisture accumulation. Dew formation in the dry buckets should be rather insignificant, since the solid angle of any point in a dry bucket subtended by the clear night sky is small so radiation cooling of the inside of the bucket would be ineffective. It is difficult to explain the observed one-to-one correspondence of sulfate with calcium if it is primarily the water in the buckets that determined the amount of sulfate deposited. The idea that the calcium particles deposit in the buckets, adsorb SO_2, then convert it to sulfate is a plausible explanation of the data. The dry-bucket data pertains to calcium levels lower than those estimated to be present near an unpaved road, since the NADP/NTN sampling network sites are in locations that avoid significant local sources of dust The central issue addressed here reduces to whether the cited correlation between calcium and sulfate holds closer to the road where the calcium levels are higher. If the trend holds, then a strong case is made for the dust from unpaved roads being a major factor in the removal of SO_2 from the atmosphere.

Conclusion

The supposition is presented that calcium carbonate rich road dust deposits across the landscape and acts as a sink for the dry deposition of SO_2. Calculations show that on a national basis a large fraction of the landscape is impacted by dust emissions, and that enough alkaline material is emitted to match the total anthropogenic SO_2 emissions. NADP/NTN dry bucket data is cited to show that in the eastern states most of the dry deposited calcium is converted to $CASO_4$ during each 8-week dry-bucket sampling period. There are indications that a significant part of the $CACO_3$ in deposited particulate can be converted to $CASO_3$ per day. A questions remains as to the efficiency of conversion of the available calcium under high alkaline loadings that occurs close to a graveled road. The main effect of the mechanism, from the standpoint of SO_2 dry deposition, is predicted to be a smoothing out the large diurnal variations caused by plant stomata closing at nighttime.

References

1. Chamberlain, A.C., 1980: Dry Deposition of Sulfur Dioxide. In: D.S. Shriner. C.R.Richmond, and S.E. Lindberg, Editors, Atmospheric Sulfur Deposition: Environmental Impact and Health Effects. Ann Arbor Science Publishers. Inc.. Ann Arbor, MI, pp 185-197.

2. O'Dell ,R.A, Mansoor Taheri, and R.L. Kabel, (1977): A Model for the Uptake of Pollutants by Vegetation. J. of the Air Pollution Control Association. 27, 1104-1109.

3. Barnard, W. R., G. J. Stensland, and D. F. Gatz, 1986: Alkaline Materials Flux from Unpaved Roads: Source Strength, Chemistry and Potential for Acid Rain Neutralization. Water. Air and Soil Pollution. 30: 285-293.

4. Williams, A.L., G.J. Stensland, D.F. Gatz, and W.R. Barnard, 1988: Development of a PM10 Emission Factor from Unpaved Roads. Preprint 88-71.4 in the Proceedings of the 81st Air Pollut. Control Assoc. Annual Meeting, Dallas, TX, 11 pp. SWS Reprint 839.

5. Williams, A.L. and GJ. Stensland, 1989: "Uncertainties in Emission Factor Estimates of Dust from Unpaved Roads" Paper 89-24.6 to be presented at the 82nd Annual meeting of the Air and Waste management Assoc, in Anaheim, Ca, June 21-24.

6. Barnard, W.R., G.J. Stensland, and D.F. Gatz, 1987: Evaluation of Potential Improvements in the Estimation of Unpaved Road Fugitive Emission Inventories. Preprint 87-58.1 in the Proceedings of the 80th Air Pollut. Control Assoc. Annual Meeting, New York, NY, 16 pp. SWS Reprint 808.

7. Williams A.L. and G.J. Stensland: The Scavenging of Sulfur Dioxide by Dry Deposited Road Dust, Paper presented at 1989 EPA/AMWA International Symposium on Measurement of Toxic and Related Air Pollutants in Raleigh, NC, May 1-5, 1989.

8. Stensland G.J. and A.L. Williams: Dry Deposited Road Dust as a Major Sink of Atmospheric Sulfur Dioxide: Paper presented at the 1989 Spring meeting of the American Geophysical Union in Baltimore, MD, May 7-12, 1989.

9. Gillette, D.A., G.A. Stensland, A.L. Williams, P.C Sinclair, and T. Z. Marquardt: Emissions of Alkaline Elements Calcium, Magnesium, Potassium, and Sodium from Open Sources in the Contiguous United States, submitted to Global Geochemical Cycles

10. Sehmel, G. A., 1983: Particle Dry Deposition Measurements with Dual Tracers in Field Experiments. In: H. R. Pruppacher, R. G. Semonin, and W. G. N. Slinn, Editors, Precipitation Scavenging. Dry Deposition, and Resuspension. Elsevier Science Publishing Co., New York, pp 1013-1025.

11. Simpson, C L., 1961: Estimates of Deposition of Matter from a Continuous Point Source in a Stable Atmosphere. HW-69292k Hanford Atomic Products Operation, Richland, Washington.

12. Sehmel, G. A. and W. H. Hodgson, 1976: Field Deposition Velocity Measurements to a Sagebrush Canopy. Pacific Northwest Laboratory Annual Report for 1975, Atmospheric Sciences , BNWL-2000-3, Battelle, Pacific Northwest Laboratory, Richland, Wash.

13. Start, G. E., 1970: Comparative diffusion and Deposition of Uranine Dye, Molecular Iodine Gas, and Methyl Iodide Gas. Proceedings of the Fifth Annual Health Physics Society Midyear Symposium, Idaho Falls, Idaho, November 3-6 (1970): Vol. II. pp, 463-473.

14. Start, G. E., 1970: Diffusion and Deposition Studies. in ERLTM-ARL 20, Air Resources Laboratory, Silver Springs, MD.

15. Doran, J.C. and T.W. Horst, An evaluation of Gaussian plume-depletion models with dual-tracer field measurements. Atmospheric Environment. 19:939-951, 1985.

16. U.S. Department of Transportation, Federal Highway Administration, Highway Statistics: Summary to 1975, U.S. Government Printing Office Stock # 050-001-00129-2.

17. Hicks,B.B and D.R. Matt, 1988: Combining Biology, Chemistry, and Meteorology in Modeling and Measuring Dry Deposition. Journal of Atmospheric Chemistry. 6: 117-131.

18. Hicks, B. B., M. L. Wesely, R. L. Coulter, R. L. Hart, J. L. Durham, R. E. Speer, and D.H. Stedman, 1983: An Experimental Study of Sulfur Deposition to Grassland. In: H. R. Pruppacher, R. G. Semonin, and W. G. N. Slinn, Editors, Precipitation Scavenging. Dry Deposition, and Resuspension. Elsevier Science Publishing Co., New York, pp 1013-1025.

19. Walcek, CJ., R.A. Brost, J.S. Chang, and M.L. Wesley,1986:SO_2, Sulfate and HNO_3 Deposition Velocities Computed Using Regional Landuse and Meteorological Data. Atmospheric Environment 20: 949-964.

20. Garland, J. A., 1977: The Dry Deposition of Sulfur Dioxide to Land and Water Surfaces. Proceedings of the Royal Society London. Series A. 354.

21. Judeikis, H.S., and T.B Stewart, 1976: Laboratory measurement of SO, Deposition Velocities on Selected Building Materials and Soils. Atmospheric Environment. 10: 779-776.

22. Braum, R.C, and MJ.G. Wilson, 1970: The Removal of Atmospheric Sulphur by Building Stones. Atmospheric Environment.4: 371-378.

23. Lipfert, F.W, 1989: Dry Deposition Velocity as an Indicator for SO_2 Damage to Materials. J. of the Air Pollution Control Association. 39: 446-452.

24. Lipfert, F.W., 1989: Atmospheric Damage to Calcareous Stones: Comparison and Reconciliation of Recent Experimental Findings. Atmospheric Environment 23: 415-429.

25. Butler, T. J., 1988: Composition of Particles Dry Deposited to an Inert Surface at Ithaca, New York. Atmospheric Environment. 22: 895-900.

26. Liberti, A, D. Brocco, and M. Possanzini, 1978: Adsorption and Oxidation of Sulfur Dioxide on Particles. Atmospheric Environment 12: 255-261.

27. Gatz, D.F., V.C. Bowersox, and J. Su, 1988: "Screening Criteria for NADP Dry-bucket Sample Data," Paper 88-101.6. at the 81st Annual Meeting of the Air Pollution Control Association in Dallas, TX.

28. Davidson, C.I., S.E. Lindberg, J.A. Schmidt, L.G. Cartwright, and L.R. Landis, 1985: Dry Deposition of Sulfate Onto Surrogate Surfaces. J. of Geophysical Research. 90: 2123-2130.

29. Hicks, B.B., 1986: Measuring Dry Deposition: A Re-Assessment of the State of the Art Water. Soil, and Air Pollution. 30: 75-90.

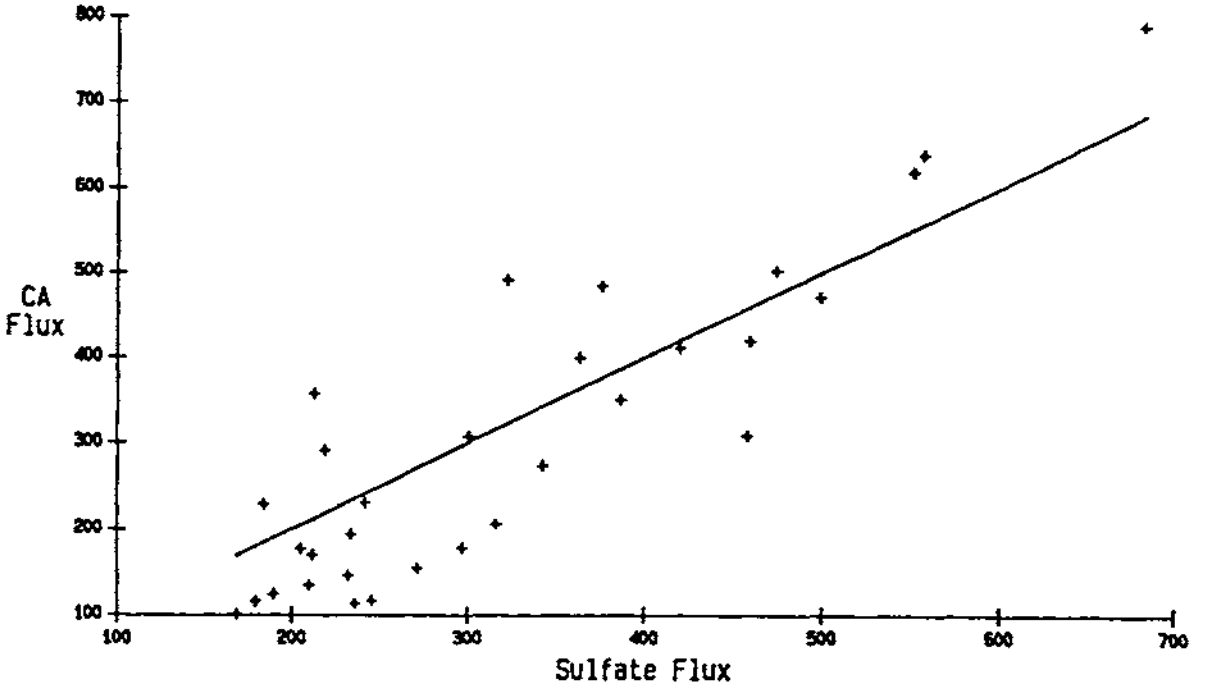


Figure 1. Ca and So_4 fluxes averaged over each of 31 eastern states in charge-equivalent units.

SENSITIVITY ANALYSES OF AREA WEIGHTED AVERAGE ALGORITHM

Jack Su and Gary J. Stensland

INTRODUCTION

It is often important to estimate environmental variables for an area when measurements are available at a limited number of points within the area. For example, it is useful to know the annual deposition of sulfate to individual states so that deposition of sulfur can be compared with annual emissions of sulfur dioxide. Such data are necessary to make informed policy decisions concerning the allocation of limited national and state resources among competing goals, such as pollution control, research, and economic growth. We have developed computer software to calculate the area weighted average of point measurements for a variable to a state or to some other user-defined region. In this chapter we present some results of the sensitivity analyses we performed on the algorithm.

METHODS AND PROCEDURES

The computer program was developed on the VAX 11/750 using standard Fortran 77. An UNIX version and an IBM PC version of the program are also available. In this chapter we will discuss the algorithm as applied to calculating deposition to states. We digitized simplified state boundaries for all 48 contiguous states of the USA using the boundaries found in the graphics package distributed by the National Center for Atmospheric Research (NCAR, 1981). This step was necessary to minimize the computational time required by the algorithm so that it could be run on a PC In this simplified scheme, each state is defined by an average of 30 points. A very small deviation in state area, less than one percent, was introduced by using the simplified boundaries.

The program itself consists of two parts. The first part reads in the data record for each site and calculate descriptive statistics for the variable of interest. This statistic along with the spatial coordinates of the data collection site are then piped into a spatial analysis routine. The spatial analysis subprogram interpolates the values of the environmental variable at the sites to the corners of each grid square. Any spatial analysis algorithm will suffice; some examples include Laplacian smoothing splines, optimum interpolation, and Krieging. We implemented an objective analysis scheme developed by Barnes (Barnes, 1964) and modified by Achtemeier (Achtemeier, et a., 1977). The second part of the algorithm reads in the digitized state boundaries and integrate the spatial field over each state to solve for the state area weighted average. The algorithm was described in detail in the last progress report.

RESULTS OF SENSITIVITY ANALYSES

We have performed a number of sensitivity analyses to ascertain how initial conditions and parameter settings affect the results produced by our program. What follows is a general discussion and results from two tests.

We chose a five year subset of screened wet deposition data from the National Atmospheric Deposition Program / National Trends Network as our test case. We used valid NADP/NTN samples and applied the following screening criteria. First, the sample must have been collected between October 1983 and October 1988. Second, samples from a given site were included only if each of the following site-dependent variables are greater than 67 percent: 1) percent precipitation coverage, defined as the ratio of the number of days of valid precipitation sampling divided by the number of days in the summary period (5 years in this case), 2) percent valid chemistry coverage, defined as the ratio of the number of days of valid chemistry sampling divided by the number of days in the summary period, 3) percent valid chemistry

precipitation, defined as the ratio of the total amount of precipitation in the summary period where we have valid chemistry data divided by the total amount of precipitation in the summary period, and 4) catch efficiency, defined as the ratio of the total amount of precipitation collected by all the samples, valid and invalid, divided by the total amount of precipitation in the summary period. From the screened data set, we calculated annual deposition values for each site for all the ions. This was done by taking the product of the weekly volume weighted average concentration and the total precipitation collected over the summary period, and then divided by the number of years of valid precipitation sampling in the summary period. For all of our subsequent analysis we used the annual sulfate deposition value at these sites. The other ions have different spatial patterns and thus the results will vary somewhat from ion to ton. For example, sodium ion is very high near the coasts and decreases rapidly inland.

There are three area in our algorithm where the results may be sensitive to initial conditions. First is the variability of the spatial pattern of the input data, which is network dependent. For long-term, wide-area, atmospheric deposition data, such as one from NADP/NTN , it is unlikely that the same sites are included int he analysis for each year. This may be due to site relocation, opening and closure, lack of rain, or too many invalid samples being collected.

The second source of variation is the way we initialize the objective analysis. There are three parameters in the modified Barnes schemes that we varied: (1) the number of sites nearest to the grid corner to use in the interpolation, (2) the shape of the weighing function with distance from the site to the grid corner as the independent variable, and (3) the size of the grid square used in the interpolation. Results for (1) and (3) are presented on Tables 1 and 2.

The third source of variation is directly related to our algorithm for calculating deposition to a given area. We assume that a variable is constant within the grid, namely the average of the four values at the grid corners. The constant field assumption has the effect of aliasing the true data field. This makes both grid size and grid placement important in determining the result.

Results of the sensitivity analyses are shown in tables 1 and 2. Table 1 shows the effect of varying the number of sites nearest to the grid corner that are used in the interpolation and table 2 shows the effect of varying the size of the grid square. In general, varying these parameters had little impact on the estimate of the annual sulfate deposition to a state. Changing the number of nearest site to use in the interpolation procedure produced 1 percent or less change in the result, except for Nevada. Changing the size of the grid square has a larger effect Depending on the state, the differences may be as large as 6 percent in annual sulfate deposition estimate. Grid size, however, should be chosen intelligently. In our sensitivity analysis, we tested a grid size of 160 km which is much to large for the NADP/NTN network.

The results of the sensitivity analyses are very encouraging. The algorithm is Curly robust as long as the user choose the initial conditions wisely. The objective analysis parameter, the nearest number of sites to use in the interpolation, produces small changes in the annual sulfate deposition estimates. The exceptions are in areas where the network is sparse relative to the size of the state, such as Nevada. Changing the grid size also produce small changes, except where the constant-value-within-a-grid assumption is violated. For annual sulfate deposition from the NADP/NTN network this occurs mostly in the East, where the gradient is large relative to the size of the grid, and where the grid size is very large relative to network density.

References

Achtemeier, G.L., P.H. Hildebrand, P.T. Schickedanz, B. Ackerman, S.A. Changnon, R.G. Semonin, "Illinois precipitation enhancement program design and evaluation techniques for high plains cooperative program," Ill. State Water Survey Final Report on Contract 14-06-D-7197, Appendix B (1977).

Barnes, S.L., "A technique for maximizing details in numerical weather map analysis," J. Appl. Meteorol., 3, 396-409 (1964).

"The SCD Graphics Utilities," NCAR technical Note, NCAR-TN/166+1A, (1981).

TABLE 1.

S04 deposition 1n Kg/Hectare/Tear

Grid size = 20 Km
Shape paraaeter of the weighting function = .5

	Number of Sites Used to Interpolate					Percentage Difference From Base Case			
			BASE CASE						
state	3 sites	4 sites	5 sites	6 sites	7 sites	3 sites	4 sites	6 sites	7 sites
AL	16.28	16.27	16.25	16.27	16.32	0.20%	0.12%	0.11%	0.41%
AR	17.02	17.02	17.02	17.01	16.97	0.00%	0.02%	-0.05%	-0.27%
AZ	3.48	3.47	3.47	3.47	3.47	0.36%	0.13%	0.08%	-0.01%
CA	2.51	2.52	2.52	2.52	2.52	-0.57%	0.10%	-0.05%	-0.20%
CO	3.54	3.54	3.55	3.56	3.57	-0.34%	-0.17%	0.31%	0.54%
CT	25.97	25.99	26.02	26.05	26.08	-0.19%	-0.11%	0.09%	0.22%
DE	23.02	23.08	23.19	23.31	23.39	-0.73%	-0.47%	0.48%	0.83%
FL	14.31	14.32	14.31	14.27	14.24	0.01%	0.08%	-0.24%	-0.45%
GA	16.72	16.76	16.78	16.79	16.79	-0.33%	-0.14%	0.05%	0.07%
IA	14.42	14.43	14.43	14.43	14.42	-0.06%	-0.02%	-0.02%	-0.06%
ID	2.05	2.05	2.04	2.04	2.04	0.47%	0.25%	-0.02%	-0.05%
IL	22.49	22.49	22.47	22.46	22.46	0.08%	0.09%	-0.07%	-0.07%
IN	26.11	26.11	26.09	26.10	26.11	0.10%	0.07%	0.04%	0.07%
KS	9.56	9.55	9.55	9.55	9.54	0.09%	0.06%	-0.02%	-0.05%
KY	23.32	23.36	23.38	23.42	23.45	-0.22%	-0.09%	0.17%	0.31%
LA	15.73	15.71	15.69	15.68	15.65	0.22%	0.12%	-0.10%	-0.30%
MA	24.07	24.06	24.06	24.07	24.09	0.03%	-0.02%	0.03%	0.11%
MD	25.03	25.03	25.07	25.12	25.16	-0.17%	-0.15%	0.20%	0.38%
ME	15.13	15.10	15.09	15.08	15.07	0.28%	0.04%	-0.04%	-0.16%
MI	25.21	25.19	25.16	25.14	25.12	0.21%	0.10%	-0.10%	-0.18%
MN	8.54	8.53	8.52	8.52	8.51	0.27%	0.07%	-0.05%	-0.17%
MO	18.07	18.08	18.07	18.07	18.07	0.00%	0.01%	-0.02%	-0.03%
MS	15.97	15.98	15.98	15.99	16.00	-0.06%	-0.01%	0.06%	0.10%
MT	2.34	2.33	2.33	2.34	2.34	0.31%	0.04%	0.23%	0.46%
NC	18.76	18.75	18.71	18.72	18.73	0.26%	0.17%	0.02%	0.09%
ND	3.70	3.71	3.72	3.73	3.74	-0.74%	-0.37%	0.24%	0.39%
NE	7.35	7.35	7.35	7.32	7.28	0.03%	0.07%	-0.36%	-0.85%
NH	20.57	20.57	20.61	20.63	20.63	-0.21%	-0.19%	0.11%	0.08%
NJ	28.24	28.20	28.15	28.09	28.02	0.31%	0.18%	-0.24%	-0.47%
NM	5.34	5.34	5.34	5.34	5.34	0.03%	0.11%	-0.03%	0.00%
NV	1.84	1.85	1.87	1.89	1.90	-1.65%	-0.80%	0.99%	1.71%
NY	28.34	28.34	28.34	28.35	28.37	-0.01%	-0.01%	0.02%	0.10%
OH	27.64	27.66	27.67	27.69	27.69	-0.11%	-0.05%	0.06%	0.08%
OK	11.52	11.51	11.50	11.51	11.53	0.20%	0.09%	0.13%	0.29%
OR	2.72	2.72	2.72	2.71	2.70	-0.02%	0.25%	-0.33%	-0.59%
PA	32.09	32.07	32.04	32.04	32.11	0.17%	0.11%	0.01%	0.21%
RI	24.05	23.97	23.92	23.89	23.89	0.56%	0.23%	-0.11%	-0.09%
SC	18.39	18.43	18.45	18.46	18.46	-0.35%	-0.12%	0.05%	0.05%
SD	4.91	4.93	4.94	4.95	4.95	-0.68%	-0.31%	0.19%	0.19%
TN	22.86	22.81	22.75	22.70	22.65	0.46%	0.24%	-0.25%	-0.44%
TX	8.34	8.33	8.33	8.34	8.36	0.21%	0.03%	0.18%	0.43%
UT	3.57	3.55	3.54	3.55	3.55	0.71%	0.12%	0.11%	0.21%
VA	22.60	22.57	22.58	22.60	22.63	0.12%	-0.05%	0.09%	0.22%
VT	22.69	22.68	22.68	22.66	22.64	0.03%	0.00%	-0.07%	-0.15%
WA	5.60	5.60	5.61	5.63	5.64	-0.14%	-0.22%	0.30%	0.47%
WI	13.92	13.92	13.90	13.89	13.88	0.11%	0.13%	-0.12%	-0.21%
WV	30.91	30.99	31.01	30.97	30.91	-0.31%	-0.06%	-0.11%	-0.31%
WY	2.90	2.90	2.90	2.90	2.90	-0.01%	0.15%	-0.05%	-0.13%

TABLE 2.

SO4 deposition 1n Kg/Hectare/Tear

6 nearest sites used to interplate
Shape parameter of the weighting function = .5

	Grid Size					BASE CASE	Percentage Difference From Base Case				
state	160 km	120 km	100 km	80 km	40 km	20 km	160 km	120 km	100 km	80 km	40 km
AL	16.59	16.79	16.42	16.33	16.26	16.25	2.07%	3.36%	1.05%	0.49%	0.05%
AR	16.56	16.76	16.83	17.02	17.03	17.02	-2.67%	-1.54%	-1.14%	0.02%	0.05%
AZ	3.49	3.45	3.50	3.46	3.46	3.47	0.57%	-0.65%	0.75%	-0.34%	-0.20%
CA	2.44	2.45	2.48	2.50	2.52	2.52	-3.11%	-2.70%	-1.50%	-0.93%	0.00%
CO	3.73	3.56	3.57	3.59	3.56	3.55	4.98%	0.43%	0.56%	1.22%	0.35%
CT	26.91	25.85	26.07	26.17	26.08	26.02	3.42%	-0.67%	0.20%	0.56%	0.22%
DE	23.95	24.17	24.23	23.78	23.24	23.19	3.27%	4.20%	4.46%	2.51%	0.20%
FL	14.28	13.97	14.18	14.42	14.28	14.31	-0.16%	-2.34%	-0.87%	0.83%	-0.21%
GA	15.93	17.05	16.69	16.77	16.82	16.78	-5.07%	1.60%	-0.54%	-0.08%	0.25%
IA	14.28	14.31	14.40	14.39	14.42	14.43	-1.04%	-0.80%	-0.23%	-0.26%	-0.04%
ID	2.09	1.94	2.03	2.05	2.04	2.04	2.60%	-5.20%	-0.35%	0.25%	-0.16%
IL	21.84	22.00	22.26	22.30	22.37	22.47	-2.82%	-2.11%	-0.94%	-0.75%	-0.48%
IN	25.61	25.90	26.06	25.99	26.08	26.09	-1.82%	-0.72%	-0.11%	-0.39%	-0.02%
KS	9.56	9.50	9.52	9.53	9.54	9.55	0.05%	-0.54%	-0.25%	-0.18%	-0.07%
KY	23.45	23.58	23.61	23.62	23.44	23.38	0.33%	0.87%	1.02%	1.05%	0.28%
LA	15.65	15.61	15.72	15.63	15.71	15.69	-0.29%	-0.52%	0.16%	-0.39%	0.09%
MA	23.33	24.57	23.18	24.02	24.09	24.06	-3.04%	2.10%	-3.69%	-0.18%	0.10%
MD	26.57	24.60	27.22	25.33	25.41	25.07	5.99%	-1.86%	8.59%	1.03%	1.37%
ME	15.93	15.04	15.34	15.32	15.12	15.09	5.58%	-0.34%	1.65%	1.50%	0.23%
MI	24.25	24.47	24.73	25.01	25.13	25.16	-3.61%	-2.73%	-1.71%	-0.60%	-0.11%
MN	8.32	8.37	8.51	8.45	8.52	8.52	-2.37%	-1.79%	-0.07%	-0.79%	-0.05%
MO	17.89	18.07	18.03	18.06	18.07	18.07	-1.00%	-0.01%	-0.22%	-0.06%	-0.02%
MS	16.38	16.03	16.24	15.93	15.99	15.98	2.53%	0.33%	1.62%	-0.29%	0.04%
MT	2.35	2.33	2.33	2.34	2.33	2.33	0.89%	0.09%	-0.05%	0.26%	0.06%
NC	19.08	18.73	18.70	18.82	18.71	18.71	1.93%	0.11%	-0.09%	0.57%	0.00%
ND	3.92	3.65	3.75	3.76	3.73	3.72	5.44%	-1.86%	0.86%	1.09%	0.30%
NE	7.20	7.20	7.27	7.28	7.33	7.35	-2.04%	-1.93%	-1.06%	-0.88%	-0.16%
NH	21.02	20.80	19.59	20.73	20.63	20.61	1.97%	0.92%	-4.93%	0.60%	0.08%
NJ	27.76	27.76	27.31	27.82	28.05	28.15	-1.44%	-1.40%	-2.99%	-1.17%	-0.38%
NM	5.43	5.31	5.35	5.35	5.33	5.34	1.71%	-0.44%	0.14%	0.31%	-0.14%
NV	1.89	1.90	1.89	1.90	1.87	1.87	1.28%	1.84%	1.23%	1.89%	0.20%
NY	28.92	29.45	28.40	28.56	28.43	28.34	2.05%	3.91%	0.19%	0.76%	0.30%
OH	28.23	28.06	28.05	27.85	27.65	27.67	2.01%	1.39%	1.38%	0.66%	-0.08%
OK	11.00	11.57	11.47	11.34	11.53	11.50	-4.33%	0.64%	-0.25%	-1.34%	0.29%
OR	2.69	2.74	2.69	2.70	2.75	2.72	-1.02%	0.90%	-1.03%	-0.74%	1.31%
PA	30.82	31.66	31.59	31.66	31.98	32.04	-3.80%	-1.17%	-1.39%	-1.19%	-0.19%
RI	24.66	24.31	24.56	24.12	24.20	23.92	3.10%	1.63%	2.68%	0.85%	1.18%
SC	18.18	18.71	18.24	18.47	18.46	18.45	-1.49%	1.40%	-1.17%	0.09%	0.03%
SD	5.17	5.01	4.97	4.94	4.93	4.94	4.55%	1.28%	0.66%	-0.02%	-0.33%
TN	20.94	22.14	21.95	22.34	22.69	22.75	-7.94%	-2.67%	-3.50%	-1.80%	-0.25%
TX	8.32	8.40	8.33	8.36	8.33	8.33	-0.06%	0.84%	0.03%	0.38%	0.10%
UT	3.23	3.37	3.44	3.53	3.53	3.54	-8.74%	-4.84%	-2.90%	-0.50%	-0.48%
VA	23.06	22.90	22.42	23.60	22.49	22.58	2.15%	1.44%	-0.67%	0.55%	-0.40%
VT	21.26	21.93	21.97	22.23	22.60	22.68	-6.28%	-3.32%	-3.12%	-1.99%	-0.36%
WA	5.51	5.69	5.60	5.47	5.61	5.61	-1.78%	1.52%	-0.20%	-0.56%	0.09%
WI	13.91	13.86	14.08	13.98	13.94	13.90	0.04%	-0.30%	1.24%	0.56%	0.26%
WV	29.71	29.71	29.92	30.44	31.03	31.01	-4.18%	-4.18%	-3.52%	-1.83%	0.08%
WY	2.93	2.88	2.90	2.89	2.90	2.90	0.99%	-0.58%	-0.03%	-0.37%	0.03%

A FIRST LOOK AT DATA TO EXAMINE THE STABILITY OF MAJOR INORGANIC IONS IN RAIN SAMPLES IN CENTRAL ILLINOIS

Van C Bowersox and Mark E. Peden

Introduction

At the recent meeting of Multistate Atmospheric Power Production Pollution Study (MAP3S) scientists in Bethesda, MD, in April of this year, workshop sessions were held to highlight major accomplishments of MAP3S research over the last 10+ years, as well as important research needs of the future. Under research needs, one topic that received extensive discussion was the question of sample stability. Are event or daily samples chemically stable? Are the changes in concentrations of the major inorganic ions small over the daily (or event) sampling period used at MAP3S sites? Are chemical changes effectively arrested by refrigeration? Apart from the addition of TCM (a preservative for dissolved SO_2) to a sample aliquot used only for S(IV) analyses, the only routine sample preservation procedure employed in the MAP3S network is refrigeration. What happens to the chemistry of a sample left in the sampler at ambient temperatures in the summer? The consensus of the group of researchers was that we do not know enough about the short term changes in the chemistry of samples held for 24-48 hours with no added preservative.

Over the last 10-15 years, there have been at least seven published studies in which event or daily samples have been compared to weekly, bi-weekly, and monthly samples - see Galloway and Likens (1976), Madsen (1982), Chan et al. (1983), Sisterson et al. (1985), de Pena et al. (1985), Topol et al. (1987), and Vet et al. (1988). While these studies have addressed differences observed between the several standard sampling protocols employed in major networks today, they only indirectly tested for sample stability, since sample change in the shortest duration samples was not explicitly investigated. These studies were done in geographically diverse regions such as southern Canada, the Midwestern U.S., the Northeast, and the Southeast A wide variety of climate conditions, soil types, and air quality conditions was encountered. Laboratories, sample handling procedures, collection equipment, and collection procedures were all different Nevertheless, with the exception of the de Pena et al. (1985) study, there was general agreement in the direction, if not the magnitude, of the differences observed. First, the alkaline earth and alkali metals, Ca, Mg, Na, and K had larger concentrations in weekly or monthly samples than in daily or event samples. On the whole, Ca and Mg differences were largest, varying from 10-35%. Na and K differences were much less consistent than Ca and Mg differences, perhaps because these elements are affected by contamination from human handling (Na) and from organic debris (K), such as leaves. Next, SO_4 and NO, differences were less than 10%, with a tendency for higher concentrations in longer duration samples. In general, SO_4 and NO, showed the smallest differences, i.e. the greatest stability, of the ions compared. Finally, the direction of H and NH_4 differences was opposite to that of the metallic cations. H and NH_4 were lower in weekly and monthly samples than in daily or event samples (Sisterson, et al., 1985). In one study NH_4 concentrations, averaged over a whole year, were 30% larger in event samples than in weekly samples. One could infer that while the metallic cations rise in concentration with time, the NH_4 concentrations fall. Since these are all alkaline elements in precipitation, to some extent these changes compensate one another stoichiometrically. One could also posit that the tendency for H-ion to drop suggests that the rise in Ca and Mg often exceeds the loss of NH_4. In fact, none of these studies tested this hypothesis directly. Further, these studies did not address the loss of free acidity due to the degradation of weak acids, though some authors concluded that this must be the cause of H-ion loss.

Methods

A study was designed to examine the stability of the chemistry of samples from a summer rain event. Major inorganic cations and anions were the focus of this study, since these all are reported by the networks presently in operation in North America. In a previous study, Peden and Skowron (1978) had found that bulk deposition samples exhibited large changes in Ca and Mg when left unfiltered at about

25C. The present study, however, focused on wet-only deposition samples, which contain much less dry deposited soil than bulk samples, because exposure is limited to the occurrence of precipitation.

Two types of samples were collected, an event sample and sequential samples. A wet/dry deposition collector of the same design and manufacture as the one used in the MAP3S and NADP/NTN networks was used to collect the event sample. Sequential samples were collected using a sampler designed and built by Northrup Services, Inc., under contract to the U.S. Environmental Protection Agency. This sampler was set to collect wet-only samples sequentially with every .03" of rainfall Collected samples were stored in 50 mL polyethylene vials kept in a chamber that was thermostatically controlled to maintain a T of – 4 C. A more detailed description of the sequential sampler can be found in Bowersox (1988) or can be obtained from Bromberg (1988).

Both the event sample and the set of sequential samples were covered and removed from their respective collectors at the end of the rain event The event sample was neither refrigerated nor filtered, while the sequential samples were cooled to 4 C as they were collected and they were kept refrigerated until removal from the collector. No other sample preservation steps were taken.

Once removed from the collectors, all of the samples were weighed to determine sample volume. Since the net volume of each sequential sample was about 35mL, it was decided to combine the water from every two vials into a single sample. This would allow adequate volume to make a series of daily measurement over about seven days. These composite samples were stored in polyethylene bottles at room temperature (20-22 C). Water from the event sample was swirled in the collection bucket and two aliquots of about 70 mL each were poured from the bucket into polyethylene bottles of the same type used for the sequential samples. Together with the sequential samples, these samples were submitted to the laboratory for analysis.

The first set of measurements on all samples was completed within five hours of the end of the rain event. This, set included pH, conductance, SO_4, NO_3, Cl, NH_4, Ca, Mg, Na, and K. After this first set of measurements was completed, a second full set of measurements was made within 24 hours of the end of the event Measurements were then done for most analytes every day through day four (a Friday) and then again on days six and seven (Monday and Tuesday).

Results

A line of convective showers passed through the Champaign-Urbana, IL area on 22 August 1989. Rain began at 0510 and continued through 0940. Two showers were received during this 4-1/2 hour period, a light shower that tapered to a drizzle by about 0640 and a thunderstorm that commenced at 0815 and continued to the end of the rain period. Rain rates during the first shower were —0.2 inches/hour, while during the thunderstorm that followed, the rain rate reached 3-5 inches/hour during the heaviest downpour. A total of 0.86 inches of rain was collected by the event collector. Thirty-eight sequential samples were collected, yielding a depth of .022 inches/sample, on average. (Note: This was substantially less than the target of .03 inches/sample.) Combining the sequential samples, as described in the Methods section above, resulted in 19 sequential samples. Two (duplicate) event samples were added to make the total number of precipitation samples 21.

As of this writing only the results of the pH, SO_4, NO_3, and NH_4 measurements have been entered and verified in computer files. Plots of these measurements were prepared to get a first look at the results. Measurements out to about 168 hours or seven days, are shown on these plots. Most analytes were measured at least five times during the seven day period and measurements will be repeated on remaining samples on day 14 and day 21. It is important to note that pH and NH_4 were selected for display because indications were that these two measurements were changing the most SO_4 and NO, were selected because they are the predominant ions effecting the pH of acidic rain samples. Finally, Ca was not entered and plotted because changes appeared to be inconsistent and, on average, insignificant.

Figure 1 shows pH plotted with time for the 19 sequential samples and the two duplicate event samples. For this figure and the others, the event sample measurements are designated by a solid circle and a solid square. All other lines are the sequential sample measurements. The duplicate event samples have pH values within .03 pH units of one another for every measurement This is an estimate of the lower bound, then, for the laboratory and handling precision of this sample set Without exception, every pH measurement rose over the seven day period. From the figure it is obvious that the greatest increase in pH occurred in the first 24-48 hours. In general, a daily or event sample would be collected during this time period. After about 72 hours, changes in the pH were random in direction and usually less than the .03 pH unit precision limit, suggesting that the sample had reached a stable pH reading. Though it appears from the figure that the pH change was smaller at lower initial readings than at higher readings, the H-ion change tended to be larger at lower pH values than at higher values. One reason for examining the changes in chemistry of sequential samples over time was to investigate whether samples collected at the outset of the storm might exhibit a greater instability than samples collected later in time, when the sub-cloud air is (presumably) cleaner due to below-cloud scavenging. Although this information cannot be gleaned from Figure 1, the data do not show any evidence that samples during any part of the storm are more or less stable than any others. For the two event samples, the free H-ion concentration dropped by 10.5 μ equiv/L over the period of the measurements. This is a loss of 29% of the free acidity of these samples. For the sequential samples, the loss of free acidity was 14.0 μ equiv/L, on average.

Figure 2 shows SO_4 concentrations in the samples over the 168-hour period. The observation that SO_4 in event and weekly samples is about the same is supported by these data. There were no significant changes in SO_4 with time in this sample set Sulfate scavenged as aerosol SO_4 or as SO, converted to SO_4 in cloud droplets is a stable aqueous species, apparently requiring no special preservation techniques in rain samples of this type. S(IV) has been shown to be unstable in rain samples, but it is manifest in rain samples only during cold period months in central Illinois.

Figure 3 shows NO, concentrations with time. Like SO_4 it is relatively stable. Six samples exhibited an initial drop in concentration over the first 24 hours. Of these six, all but one were from the first shower that occurred between 0S10 and 0800. At this time it is not clear why NO, in this shower would be any more or less stable than NO, in the second shower. This feature bears further investigation.

Finally, Figure 4 displays NH_4 changes with time. As for pH, the data are consistent All samples showed a loss of NH_4, particularly during the first 48 hours. In most samples, the loss continued, but at a lower rate. On average, the sequential samples lost 43 μ equiv/L or 31% of the initial concentration. The event samples lost 53 μ equiv/L or 34% of the initial value.

The approximately 5 μ equiv/L loss of NH_4, coupled with the approximately 12 μ equiv/L loss of H-ion, indicates that these samples lost between 15 and 20 y equiv/L of free acidity. All of the cation and anion measurements together, those shown here and those not yet available in computer files, cannot stoichiometrically account for this loss of H-ion. Unmeasured and unstable ions are thus implicated as the source of this loss in free acidity. In future experiments, organic acids should be measured to assess their role in the free acidity changes in precipitation samples.

Figure 1. pH versus time for 19 sequential (.022") and 2 event samples collected on 22 August 1989 at Champaign, IL

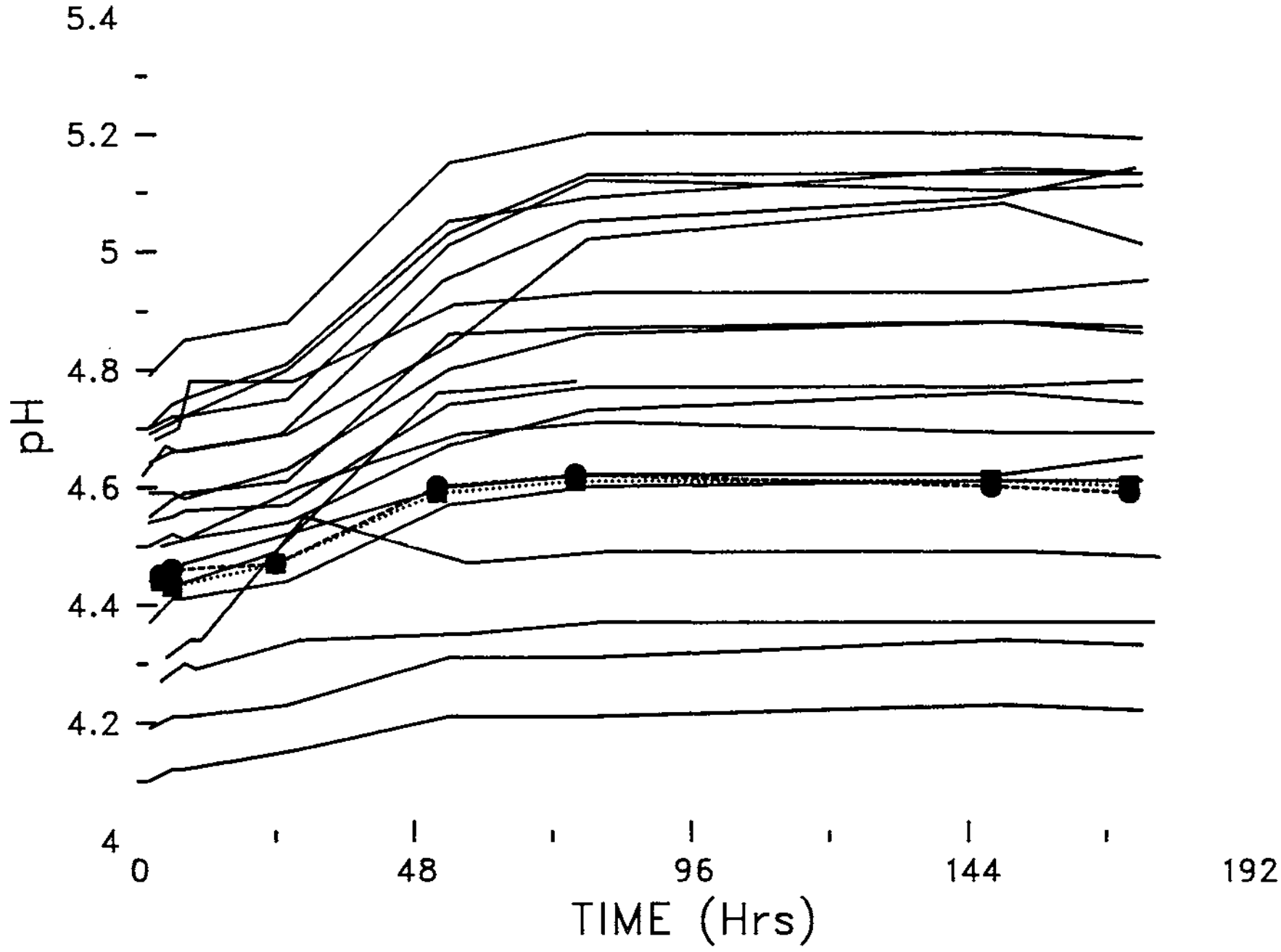


Figure 2. SO, versus time for 19 sequential (.022") and 2 event samples collected on 22 August 1989 at Champaign, IL

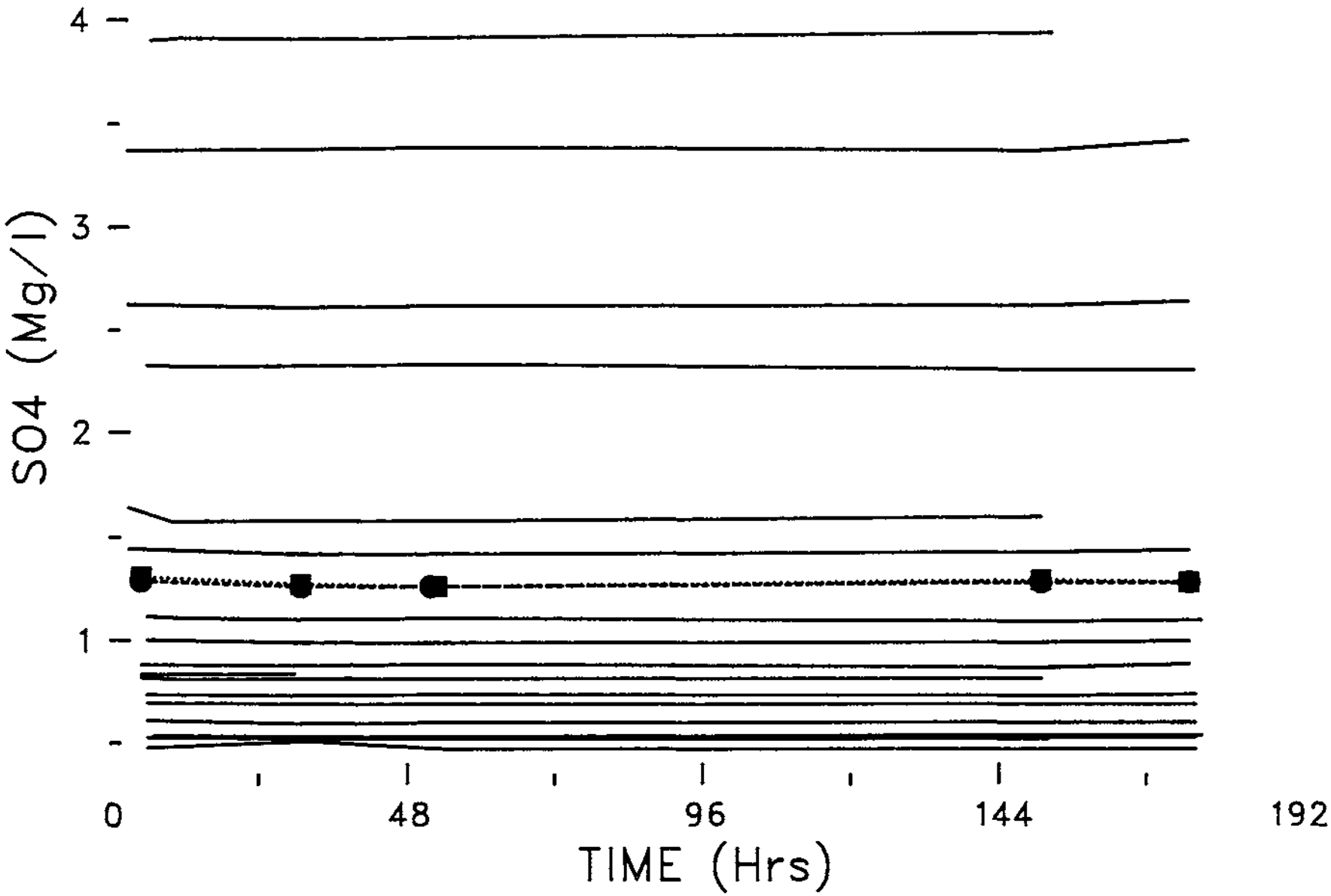


Figure 3. NO versus time for 19 sequential (.022") and 2 event samples collected on 22 August 1989 at Champaign, IL

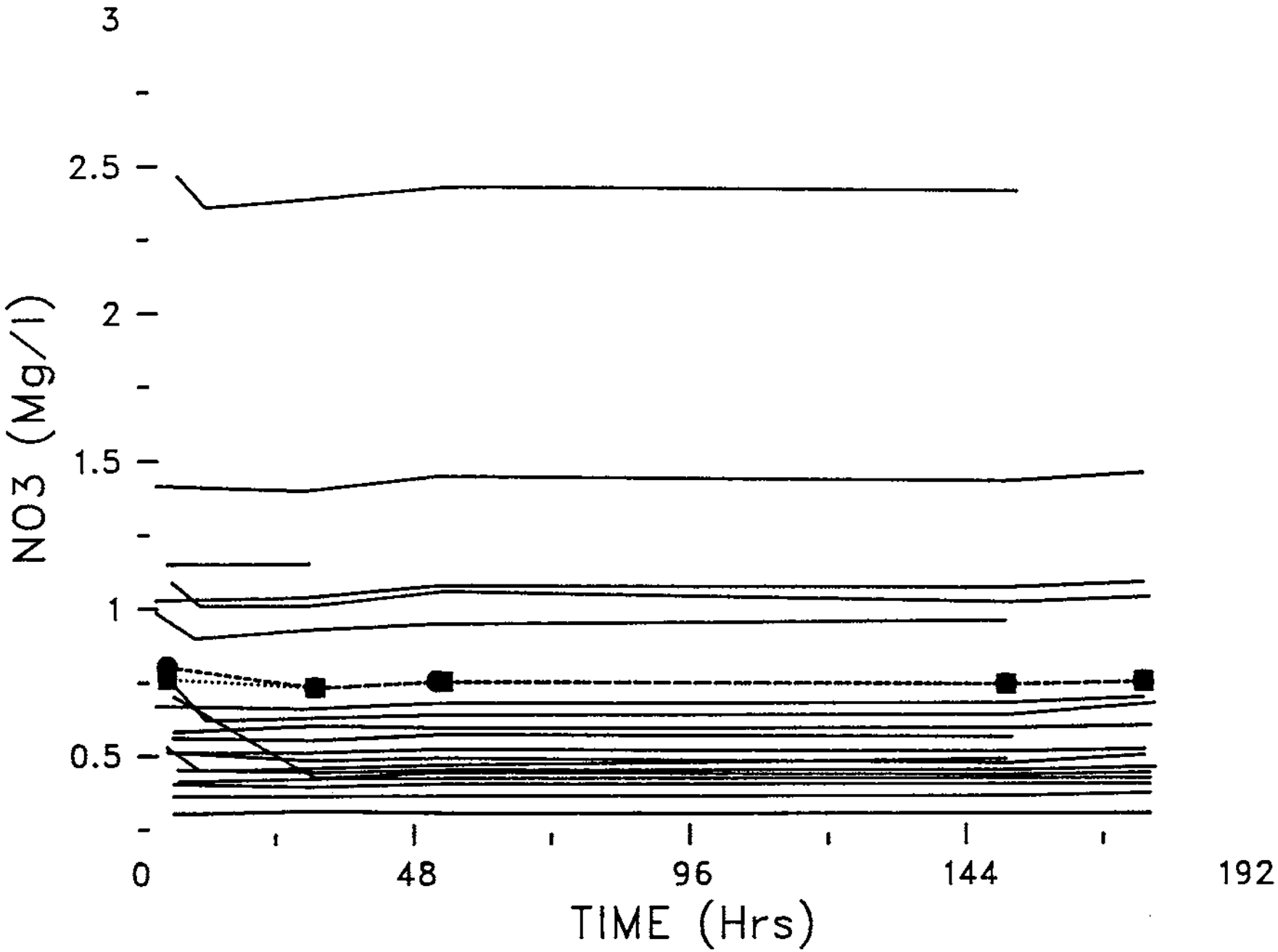
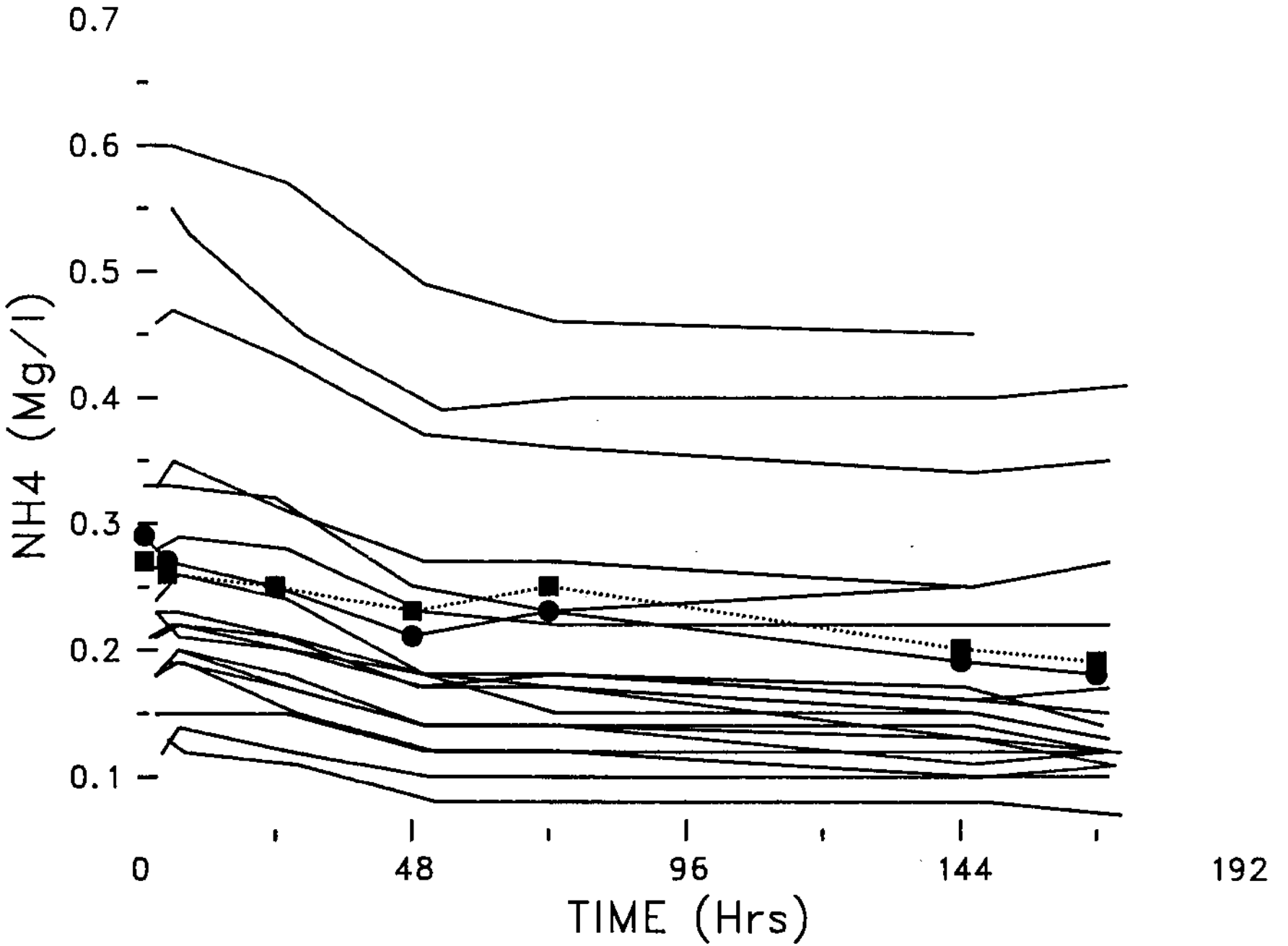


Figure 4. NH, versus time for 19 sequential (.022") and 2 event samples collected on 22 August 1989 at Champaign, IL



References

Bowersox, V.C., 1988: A Description of the Sequential chemistry of Rain Experiment - 1988, a Component of 3CPO. In: Study of Atmospheric Pollution Scavenging, Twenty-second Progress Report to the U.S. Dept. of Energy, Illinois State Water Survey, Champaign, IL pp. 3-10.

Bromberg, S., 1988: Personal communication. U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

Chan, W.H., Tomassini, F, and B. Loescher, 1983: An evaluation of Sorption properties of precipitation constituents on polyethylene surfaces. Atmos. Environ. 17:1779-1785.

de Pena, R.G., Walker, K.G, Lebowitz, L. and J.G. Wicka, 1985: Wet deposition monitoring - effect of sampling period. Atmos. Environ. 19:151-156.

Galloway, J.N. and G.E. Likens, 1976: Calibration of collection procedures for the determination of precipitation chemistry. Water. Air. Soil Pollut 6:241-258.

Madsen, B.C., 1982: An evaluation of sampling interval length on the chemical composition of wet-only deposition. Atmos. Environ. 16:2515-2519.

Peden, M.E. and L.M. Skowron, 1978: Ionic Stability of Precipitation Samples. Atmos. Environ. 12:2343-2349.

Sisterson, D.L., Wurfel, B.E., and B.M. Lesht, 1985: Chemical differences between event and weekly precipitation samples in northeastern Illinois. Atmos. Environ. 19:1453-1469.

Topol, L.E., On-Lev, M., and A.K. Pollack, 1987: Comparison of weekly and daily wet deposition sampling results. In: Johnson, R.W. and G.E. Gordon, eds. The chemistry of acid rain: Sources and Atmospheric Processes. The American Chemical Society Symposium Series No. 349. pp. 229-241.

Vet, R.J., Sirois, A., Jeffries, D.S., Semkin, R.G., Foster, N.W., Hazlett, P. and C.H. Chan, 1988: Comparison of bulk, wet-only, and wet-plus-dry deposition measurements at the Turkey Lakes Watershed. Can. J. Fish. Aquat. Sci. 45:26-37.

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LEAD AND CADMIUM LOADINGS TO THE GREAT LAKES FROM PRECIPITATION

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ABSTRACT. We present the first analysis of precipitation chemistry data from the Great Lakes Atmospheric Deposition (GLAD) network of wet-only precipitation samplers. Lake loadings were calculated from 1- or 2-yr (1982-1983) volume-weighted mean ion concentrations and 30-yr mean annual precipitation amounts, using an objective analysis method to interpolate measurements to a 40 x 40 km square grid over the Great Lakes region. The results show that atmospheric loadings of Cd, Pb, and other cations to the Great Lakes are in many cases considerably smaller than those estimated from the bulk precipitation measurements of the early 1970s. For Pb, some portion of the differences can be accounted for by the decrease in emissions that resulted from reductions in the Pb content of gasoline. Valid dry deposition in the bulk samplers also accounts for a portion of the differences. However, for the most extreme differences, contamination of the bulk collectors by resuspended local surface dust is likely to be a major cause. Good agreement was noted between the precipitation-only loadings derived from the GLAD data and those recently given by Strachan and Eisenreich (1987).
ADDITIONAL INDEX WORDS: Trace metals, atmospheric deposition, pollution load, toxic substances.

INTRODUCTION

The purpose of this paper is to report lake loadings calculated from the first U.S. wet-only precipitation chemistry measurements on the shores of the Great Lakes and to compare these loadings with previous estimates. We also discuss possible explanations for the differences, and their implications.

In 1983, the International Joint Commission's Great Lakes Water Quality Board reported that 900 chemicals and heavy metals potentially dangerous to human health and biota had been identified in the Great Lakes (USEPA 1985a). In its 1985 Report, the same Board identified 11 organic and metallic "critical pollutants" now present in the Great Lakes that can threaten human health and the aquatic ecosystem. Harmful levels of pollutants in fish tissues were observed and warnings against eating certain fish taken from Lake Michigan were issued in 1985 by the four states bordering the lake. In May 1986 the eight Great Lakes Governors signed a Toxic Substances Control Agreement, which identifies the problem of persistent toxic substances as "the foremost environmental issue facing the Great Lakes."

The average water retention times for the upper lakes are long (100 years for Lake Michigan, 180 years for Lake Superior) (DePinto *et al.* 1986), so once contaminants enter the system, most tend to stay.

Evidence has mounted over the past 1-2 decades that atmospheric transport and deposition is an important, and in some cases perhaps dominant, pathway by which certain toxic substances reach the Great Lakes. A number of industrial and urban source areas for metals and other toxic substances are located on or near the lakes, in locations where prevailing winds can transport pollutants to the lakes through the atmosphere. Further, the lakes have large surface areas, which make them susceptible to atmospheric loading of pollutants from precipitation and dry processes.

The substances for which evidence of the importance of atmospheric deposition has been presented include PCBs (Eisenreich *et al.* 1981, Murphy *et al.* 1981, Rodgers and Swain 1983, and

others), toxaphene (Rice *et al.* 1986), and metals such as Cd, Pb, and Zn (Winchester and Nifong 1971; Gatz, 1975; Eisenreich 1980, 1982; Schmidt and Andren 1984). The recent report of Strachan and Eisenreich (1987) shows atmospheric input to be the major source of PCBs, DDT, B(a)P, Dieldrin, alpha-HCH, Pb, and Cd, especially to the upper lakes. Although the evidence for an important role for atmospheric deposition is strong, additional details regarding sources, transport, and deposition mechanisms must be provided before remediation strategies can be devised. A mass balance approach has been selected to provide the overall framework within which future research will take place (USEPA 1985a).

Because atmospheric deposition already had been considered to be a major source of metals to the lakes, measurements of atmospheric inputs began in the 1970s, using bulk samplers. Bulk samplers are typically buckets or funnels open to the atmosphere at all times (Whitehead and Feth 1964). They collect materials that deposit via precipitation and dry processes. Schmidt and Andren (1984) have provided a comprehensive review of these measurements, based largely on the work of Allen and Halley (1980). Several papers not included in these reviews, but also reporting the results of bulk sampling to estimate atmospheric deposition to the Great Lakes or in the Great Lakes area, have also appeared in recent years (Chan and Kuntz 1982, Eisenreich 1980, Sanderson *et al.* 1985). Comparisons of metal deposition in bulk and wet-only precipitation samplers have also been published (Eisenreich *et al.* 1977, Sanderson *et al.* 1985).

Bulk collectors have been criticized for being prone to contamination by locally resuspended surface dust, and for their inherent uncertainties in the amounts and the representativeness of the dry-deposited fraction of their collections. As uncertainties in the dry-deposited fraction were documented (Hicks *et al.* 1980), the Great Lakes Atmospheric Deposition (GLAD) network was redirected toward measurements of wet-only deposition fluxes. Wet-only sampling began in 1981 (USEPA 1985a), and the first full calendar year of data was produced during 1982. This paper provides an analysis and interpretation of the first 2 years of GLAD data for Cd and Pb, two toxic metals largely from man-made sources and for which atmospheric inputs to the lakes are important.

METHODS

Sampling Locations

A map of GLAD and National Atmospheric Deposition Program/National Trends Network (NADP/NTN) site locations in the Great Lakes region is shown in Figure 1. Table 1 lists names, map codes, state, and county of the sampling sites in the GLAD network.

The GLAD network was established to provide measurements of wet-only atmospheric deposition (i.e., deposition in precipitation only, excluding dryfall) that may be used to estimate chemical loadings to the Great Lakes. To do this, some GLAD sites were sited in lakefront cities so deposition from industrial, transportation, and residential sources in and near urban areas could be measured. Other samplers were placed at lakeshore sites in rural areas to measure deposition from area-wide sources. In addition, one site was located in central Minnesota, about 200 km west of Lake Superior, to measure regionally representative deposition from sources largely upwind of the Great Lakes. This site satisfied the same siting criteria as NADP/NTN sites.

Wet-only samples are also collected on the Canadian side of the Great Lakes; however, these data have not been used in this assessment. Because different collectors and sample durations are used in the two countries, the Canadian and U.S. data "cannot be readily compared and used to estimate whole lake loadings" (Great Lakes Water Quality Board 1985). Further research is needed to quantify potential differences in results from these two networks. Such research should include evaluation of data, beginning in 1984, from co-located Canadian and GLAD samplers at two locations.

Sampling Methods

Collection and analysis of samples and data reporting for the GLAD network were carried out by the USEPA's Great Lakes National Program Office (GLNPO). Details of these respective procedures have been described in GLNPO documents (USEPA undated-a, USEPA undated-b); only brief descriptions are provided here.

In the GLAD network, precipitation samples were collected in AeroChem Metrics samplers, designed to collect wet-only samples by uncovering a plastic bucket only during precipitation. These buckets were lined with polyethylene bags. Field observers inspected the sampler every Tuesday at

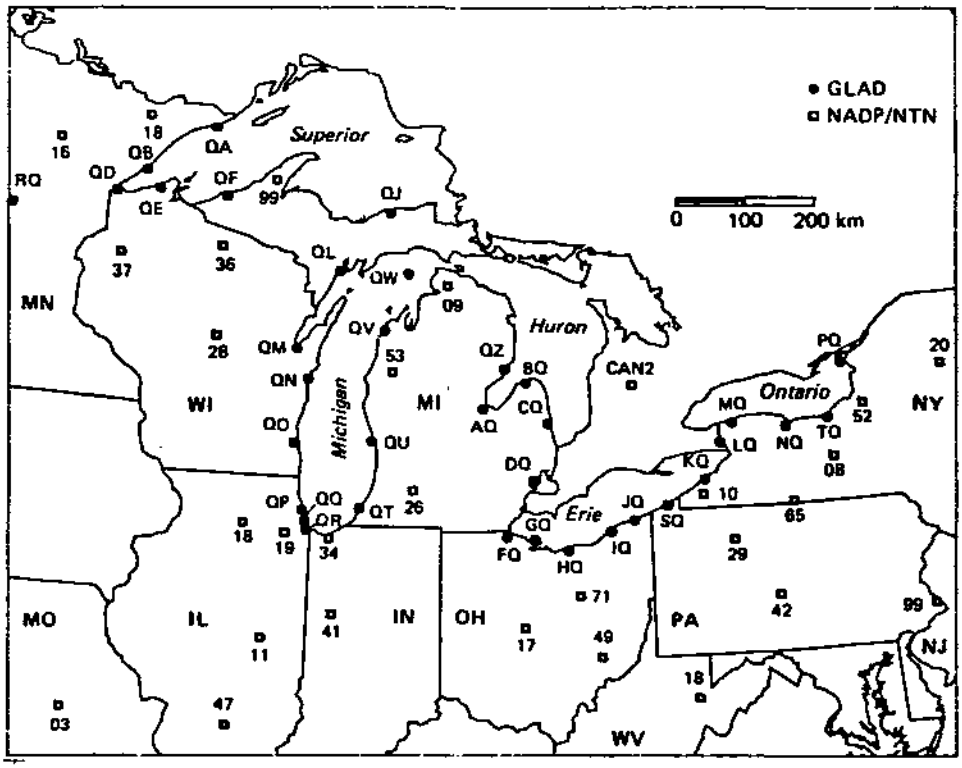

FIG. 1. Network map for GLAD and NADP/NTN sampling sites.

about 9 A.M. local time. When a bag contained 500 mL or more of liquid precipitation (or at least 1.25 in. of snow), a sample was collected and another bucket and liner installed. Samples not meeting this minimum volume were left in the field for one or more additional weeks, until sufficient sample had accumulated. Beginning in 1984, rain gauges were installed at GLAD sites, so an independent measurement of the precipitation amount was available. However, for the measurements reported in this paper, the only on-site measurement of precipitation amount was the collected volume from the AeroChem Metrics samplers.

After collection, a 20- to 40-mL aliquot of sample was decanted from the bag for field pH and conductance measurements. A half liter polyethylene bottle next was filled and shipped to the EPA analytical laboratory. Upon arrival at the laboratory, samples were stored at 4°C until 16 samples had arrived. Then samples were split and preservatives added to the two portions, as appropriate to the analysis (e.g., 5 mL of concentrated nitric acid were added per liter of the portion intended for metals analyses).

Analytical Methods

The GLAD samples were measured for Ca^{2+}, Mg^{2+}, and Na^{+} ions using the inductively coupled argon plasma (ICAP) method. Flame atomic absorption spectrophotometry (AAS) was used for K^{+} analyses, and flameless AAS for Pb and Cd analyses. Automated wet chemical methods (Technicon) were used to determine NH_4^+, NO_3^- + NO_2^-, $SO_4^=$, and Cl^-. (For the remainder of this paper, ionic charge is omitted for convenience.)

Data Screening

The criteria for including data from a GLAD or NADP/NTN sampling site in this study were that the site have valid data for at least 75% of the 2-year period and valid data representing at least 75% of the 2-year precipitation total. Since GLAD sites did not have rain gauge measurements during 1982 and 1983, it was necessary to convert sample

*TABLE 1. GLAD network sites*r.

Map code	Site Name	State/County	Valid years	Trace metals
Lake Superior				
QA	Hovland	MN, Cook	1982	No
QB	Gooseberry Falls	MN, Lake	1983	Cd only
QD	Duluth	MN, St. Louis	1982-83	Cd only
QE	Cornucopia	WI, Bayfield	1982	No
QF	Ontonogan	MI, Ontonogan	1982-83	Yes
QJ	Grand Marais	MI, Alger	1982-83	Yes
RQ	Gull Lake	MN, Crow Wing	1982-83	Yes
Lake Michigan				
QL	Escanaba	MI, Delta	1982-83	Yes
QM	Green Bay	WI, Brown	1982	No
QN	Manitowoc	WI, Manitowoc	1982-83	Yes
QO	Milwaukee	WI, Milwaukee	1982-83	Yes
QP	Evanston	IL, Cook	1982-83	Yes
QQ	Jardine Plant	IL, Cook	1982-83	Yes
QR	South Water Plant	IL, Cook	1982-83	Yes
QT	Benton Harbor	MI, Berrien	1982-83	Yes
QU	Muskegon	MI, Muskegon	1982	No
QV	Empire	MI, Leelanau	1982-83	Yes
QW	Beaver Island	MI, Charlevoix	1982	No
Lake Huron				
AQ	Bay City	MI, Bay	1982-83	Yes
BQ	Port Austin	MI, Huron	1982-83	Yes
CQ	Port Sanilac	MI, Sanilac	1982-83	Yes
DQ	Mount Clemens	MI, Macomb	1983	Yes
QZ	Tawas Point	MI, Iosco	1982-83	Yes
Lake Erie				
FQ	Toledo	OH, Lucas	1982-83	Yes
GQ	Put-In-Bay	OH, Ottawa	1982	No
HQ	Lorain	OH, Lorain	1982	No
IQ	Fairport Harbor	OH, Lake	1982-83	Yes
JQ	Ashtabula	OH, Ashtabula	1982-83	Yes
KQ	Dunkirk	NY, Chautauqua	1982-83	Yes
LQ	Grand Island	NY, Erie	1982	No
SQ	Erie	PA, Erie	1982-83	Yes
Lake Ontarior				
MQ	Olcott	NY, Niagara	1982	No
NQ	Rochester	NY, Monroe	1982-83	Yes
PQ	Cape Vincent	NY, Jefferson	1982-83	Yes
TQ	Fair Haven	NY, Cayuga	1983	No

volumes to precipitation amounts in order to calculate the 2-year precipitation total. Criteria for identifying samples having valid data were given by Gatz *et al.* (1987). If a sampling site did not meet the 2-year criteria, it was reevaluated for inclusion of 1 year's data only. The GLAD site at Copper Harbor, Keweenaw Co., Michigan, did not meet selection criteria for either year and does not appear in Table 1 or Figure 1.

Whereas NADP/NTN data reporting criteria

assure that only samples with analyses for all measured ions are available to the public, no similar requirement was placed on the GLAD data. Thus, samples appear in the GLAD data for which one or more analyses may be missing. This means that the checks for data completeness (75% of the time and 75% of the precipitation during the 2-year period) had to be applied ion by ion-for the GLAD data, instead of sample by sample, as for NADP/NTN data. This resulted in varying number of valid sites from which to calculate deposition fluxes and lake loading estimates for the various ions. A list of sites excluded from the flux calculations for the various ions was given by Gatz *et al.* (1987).

Calculation of Integrated Ion Concentrations

Some measure of the overall concentration of each ion at each sampling site is necessary for estimating long-term (annual or longer) wet deposition fluxes. For this work we used sample volume-weighted mean concentrations. These concentrations were computed for each site using the combined 2-year data set, where possible, or for individual years, where data for only 1 year were available. This method was chosen to provide overall spatial patterns of the concentrations from which to calculate deposition fluxes.

Deposition Calculations

Our objective was to estimate climate-averaged loadings of atmospheric pollutants to the five Great Lakes from precipitation alone. Ideally, the fluxes would be *measured* over a suitably long period. Unfortunately, the GLAD data set is not among the very few with such a record of measurements. Further, rain gauge measurements were not available at the GLAD sites for 1982 or 1983. Since year-to-year fluctuations in mean precipitation are likely to be greater than those in volume-weighted mean concentration, we chose to compute deposition fluxes as the product of the available short-term mean concentrations and long-term (30-year) mean precipitation values. The 30-year precipitation record available from the National Weather Service (NWS) has the added advantage that the spatial density of the measurements is much greater than that of the combined GLAD and NADP/NTN networks. Fluxes computed in this way should be better approximations of the climate-averaged loadings than those measured for 1 or 2 years.

Estimation of wet-only loadings to the lakes was a three-step process. First, 30-year mean precipitation amounts and volume-weighted mean concentrations were interpolated to the intersections of a 40 x 40 km grid over the Great Lakes region. Then deposition fluxes were computed at each grid intersection as the product of ion concentrations and precipitation depth. Finally, the calculated fluxes were integrated over the lake areas to produce annual loadings. Details of this procedure were given by Gatz *et al.* (1987), and a brief account is presented here.

For the first step, values of precipitation at the grid vertices were estimated using an objective analysis procedure developed by Achtemeier (1987) and Achtemeier *et al.* (1977), based on earlier work by Barnes (1964, 1973). These estimates are based on the nearest five measured values, weighted using a negative exponential function of distance from the grid point. The data used in this analysis were obtained from the NOAA National Climatic Center (NCC), Asheville, North Carolina. They are 30-year (1951-80) precipitation normals, which were computed as the arithmetic mean of 30 annual precipitation amounts. Station histories, documented at NCC, were used to screen all precipitation data from 1) the NWS cooperative station network, and 2) the NWS first-order station network in all states having Great Lakes shoreline. The data used in our analysis were screened by NCC to assure that instrument exposure and station location were "homogeneous" for the 30-year period. A brief description of this approach is available (National Climatic Center 1982).

Ion concentrations at the grid points were estimated in the same way, also using the nearest five measurements. The map of sampling sites is shown in Figure 1. Data from both the GLAD and NADP/NTN networks were used in the interpolations for those species measured by both networks. Cd and Pb were measured only by the GLAD network.

Interpolated concentrations and precipitation amounts were multiplied at each grid intersection to produce deposition values at each grid point. Spatial distributions of annual wet deposition fluxes were computer-plotted from these gridded values. Annual wet loadings to the lakes were estimated from the values computed for each grid box having some portion of its area over one of the lakes. A mean value for each of these boxes was computed as the arithmetic mean of the values at the vertices. Where only a portion of the box was over water, the grid-box

deposition was decreased by multiplying by the water-area/total-area ratio, so as to include only the over-water portion of the deposition.

The accuracy of the areal integration was assessed in two ways. In the first, the lake areas computed by integrating whole and partial grid boxes over the lakes were compared with values of lake area in the literature (Todd 1970). The computed lake areas were all smaller than those in the literature, but the differences were all less than 3%, probably within measurement accuracy. Nevertheless, computed fluxes were increased by the ratio of the literature area to the summed grid-box area for the respective lakes. Second, estimates of precipitation over the lakes, made using the areal integration method on the 1951-80 data, were compared against an independent estimate (Hartmann, H., Personal communication. National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Ann Arbor, Michigan, July 1986.) for a very similar 30-year period (1954-83). Except for Lake Huron, where there was a difference of about 11% (relative to the mean of the two estimates), the greatest difference was 2%.

We have examined the data for an explanation of the 11% difference for Lake Huron. The difference was not caused by unusual values during the non-overlapping years of the two data sets. Rather, it appears to be related to differences in the measurement networks. Only U.S. measurements are included in the 1951-80 data, so the objective estimates of precipitation over Georgian Bay, for example, required a considerable extrapolation away from the data domain. Such extrapolations were not required with the 1954-83 data set, which includes data from both the Canadian and U.S. sides of the lakes. The observed 11% difference in precipitation loadings to Lake Huron is a rough estimate of the lower limit of the uncertainty that may be expected in the computed trace element loadings for this lake. (Whatever uncertainty prevails for precipitation loadings, for which the measurement network is relatively dense, should be a lower limit of the uncertainty of the loadings, which incorporate concentrations measured in a much less dense network—sometimes only a few sites per lake.) Considerably less extrapolation was required for the other four lakes; thus the uncertainty of the objective method should be smaller. This appears to be the case, as evidenced by the good agreement on precipitation loadings for these lakes with the independent estimates.

Uncertainty Estimates

It is important to the understanding of the magnitude of the differences between the current wet-only estimates and the previous bulk estimates of trace element loadings of the Great Lakes that we provide some estimate of the uncertainties associated with the present loadings calculations. We take as a reasonable upper limit of the possible trace element loading to a lake, the product of the 30-year mean precipitation flux and an estimated upper limit trace element concentration.

The upper limit concentration is estimated (in a manner independent of the objective analyses) as the mean plus two standard errors, computed from the volume-weighted mean concentrations at all sampling sites associated with each lake (e.g., see Table 1). Where additional nearby sites might reasonably be included among the sites used for a given lake (e.g., site QL, at Escanaba, Michigan, might well be included in the Lake Superior sites), we computed the mean plus two standard error concentration for both alternative groups. The higher result was then taken as the upper limit concentration.

RESULTS

The first results to be presented are spatial distributions of the separate components needed to calculate wet deposition, namely Pb and Cd concentrations in precipitation and precipitation amount. Spatial patterns of Pb and Cd wet deposition are presented next. Finally, the annual wet deposition loadings of Pb and Cd to the individual lakes are presented and compared to other recent estimates.

Spatial Distribution of Metal Concentrations

Spatial distributions of Cd and Pb concentrations in precipitation are shown in Figures 2 and 3, respectively. For Cd, minimum concentrations ($< 0.2\ \mu g/L$) occurred over western Lake Superior, as well as most of Lake Huron. Cd concentrations in excess of $0.5\ \mu g/L$ occurred over mid-Lake Michigan, eastern and western portions of Lake Erie, and the western 2/3 of Lake Ontario. Pb concentrations ranged from less than $2\ \mu g/L$ over western Lake Superior to more than $8\ \mu g/L$ at the southern tip of Lake Michigan and over much of Lake Ontario.

Spatial Distribution of Precipitation

The distribution of mean annual precipitation over the Great Lakes for the 30-year period 1951-1980 is shown in Figure 4. As described in the Methods

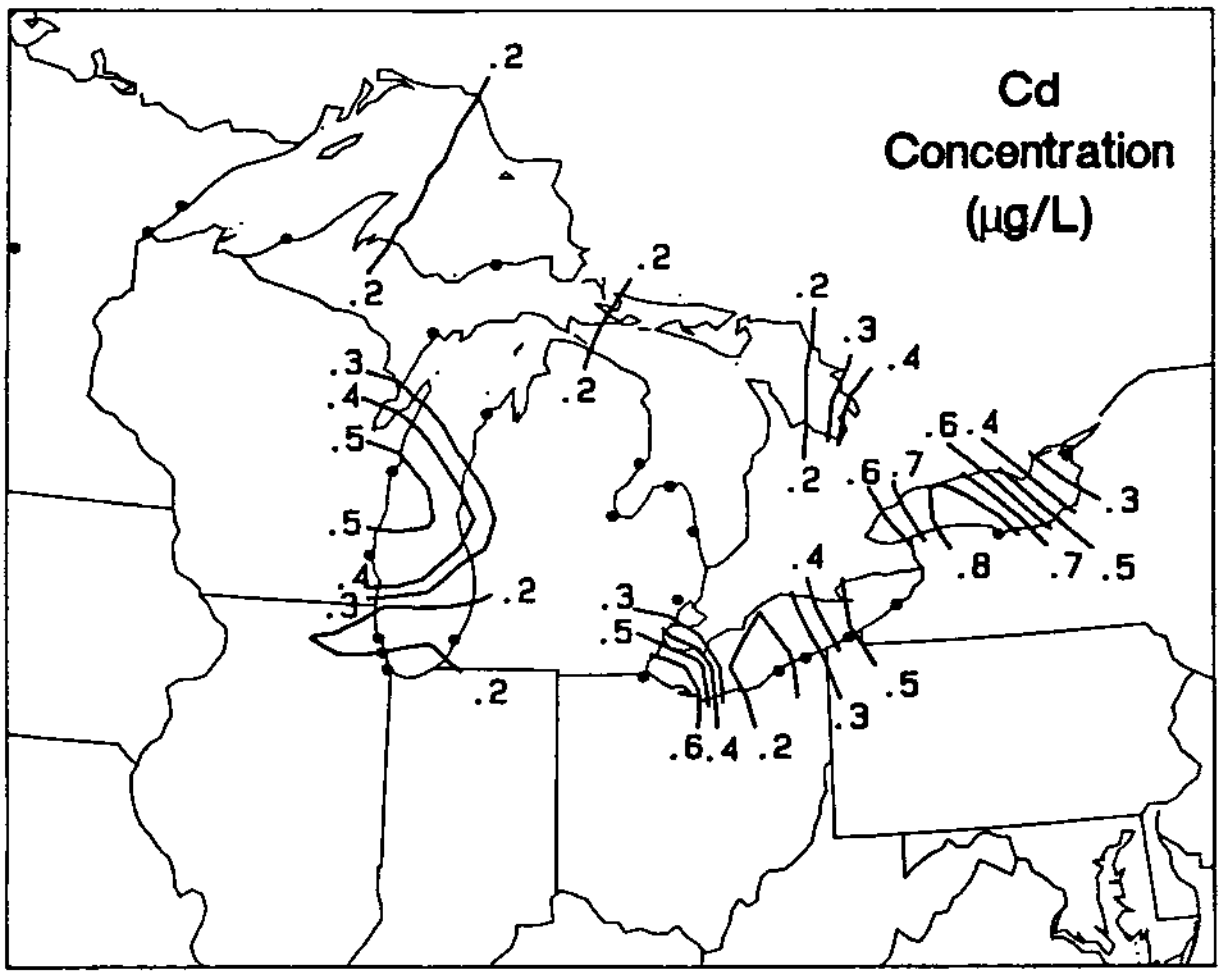

FIG. 2. Spatial distribution in total Cd concentrations in precipitation, from GLAD network data, 1983. Solid circles are sampling stations that met the data completeness criteria and were used in this analysis.

section, the contours were drawn to grid point values estimated from measurements at rain gauge sites. Precipitation in general increased from northwest to southeast, with amounts ranging from near 70 cm over northwestern Lake Superior to more than 120 cm over eastern Lake Ontario. Amounts greater than 100 cm occurred in southern Lake Michigan and eastern Lake Erie, as well.

Spatial Distributions of Wet Deposition Fluxes

Annual wet deposition fluxes of Cd and Pb, based on 1983 GLAD data only, are shown in Figure 5 and 6, respectively. GLAD network sites used in the analyses are shown in both figures. As for other spatial analyses, only data from sites meeting the screening criteria were used. The measurement networks in these two figures are slightly different for this reason. Minimum fluxes of both metals occurred in northern areas of the Great Lakes basin. Lowest measured annual Cd fluxes were about 1 g/ha, with maximum values in excess of 6 g/ha. Annual wet fluxes of Pb ranged from less than 20 to more than 100 g/ha. Maximum Cd fluxes occurred over the middle of Lake Michigan, much of Lake Ontario, and both the western and eastern extremes of Lake Erie. The largest Pb fluxes occurred in the Chicago area, eastern Lake Erie, and much of Lake Ontario.

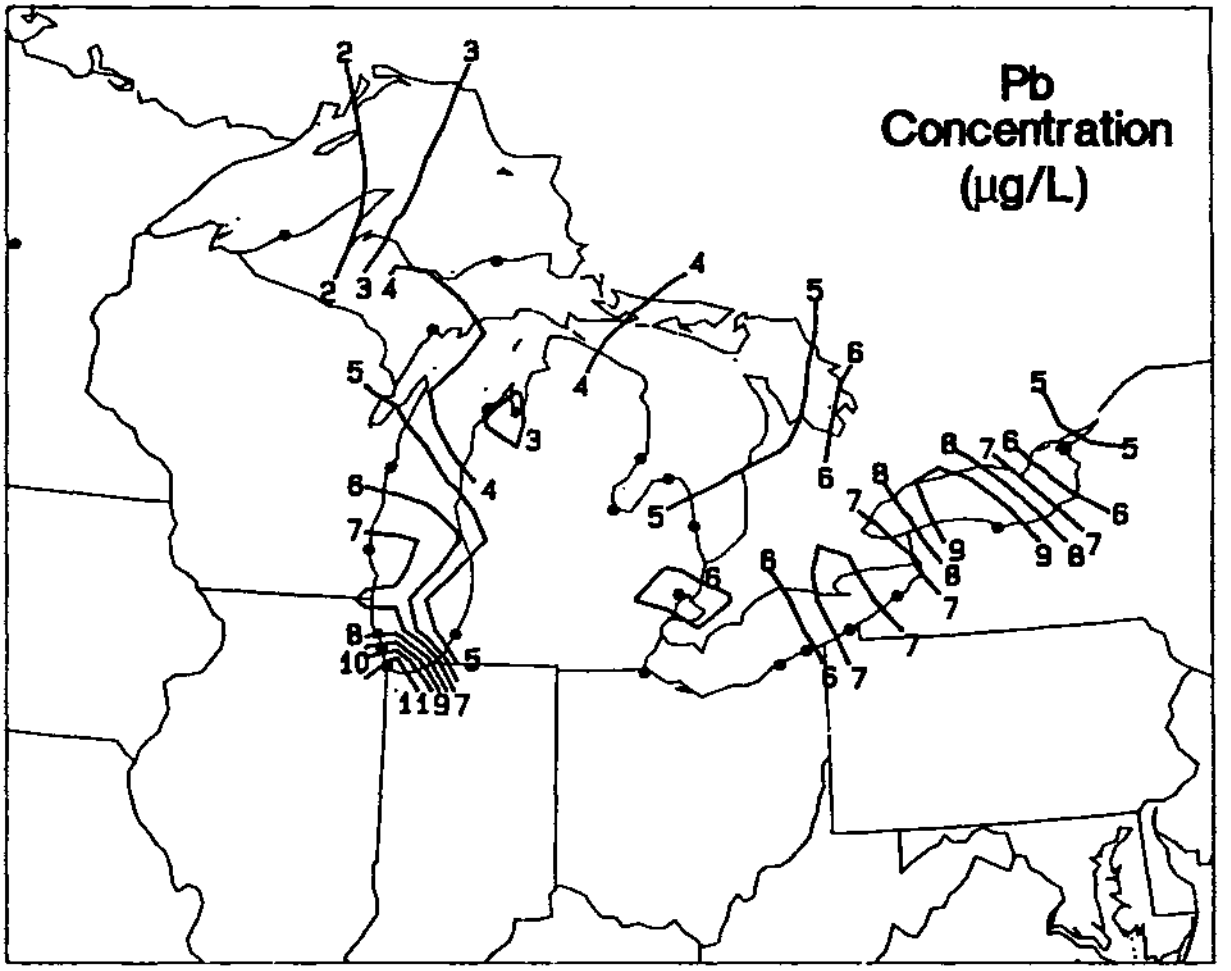

FIG. 3. Spatial distribution in total Pb concentrations in precipitation, from GLAD network data, 1983. Solid circles are sampling stations that met the data completeness criteria and were used in this analysis.

Atmospheric Loadings to the Lakes, and Comparisons to Previous Estimates

A summary of atmospheric wet-only deposition loadings to the Great Lakes is given in Table 2. Results from the objective analysis method and the independent estimate of upper limit loading are both shown. For Cd and Pb, the data set consisted of GLAD data for 1983. For the remaining elements, both GLAD and NADP/NTN data for 1982-83 were used to estimate wet-only loadings. Previous results based on mass balance modeling (Strachan and Eisenreich 1987) and on bulk precipitation measurements (Acres Consulting Services, Ltd. 1975, 1977; Eisenreich *et al.* 1977) are also given in Table 2 for comparison.

It is worth noting at this point that, except for Cd, Pb, and the nitrogen species, the atmospheric loadings of all of the species listed in Table 2 were only a few percent of the estimated non-atmospheric loadings. Data and discussions supporting this assertion were provided by Gatz *et al.* (1987).

Figures 7 and 8 provide graphical comparisons of wet-only lake loadings (both objective analysis and upper limit estimates) of Cd and Pb, as computed from the GLAD data, with wet-only and total atmospheric loadings obtained by Strachan and Eisenreich (1987) and with total atmospheric loadings from bulk precipitation sampling (1JC 1977).

For Cd (Table 2, Fig. 7), the upper limit wet-only lake loading estimates exceed the correspond-

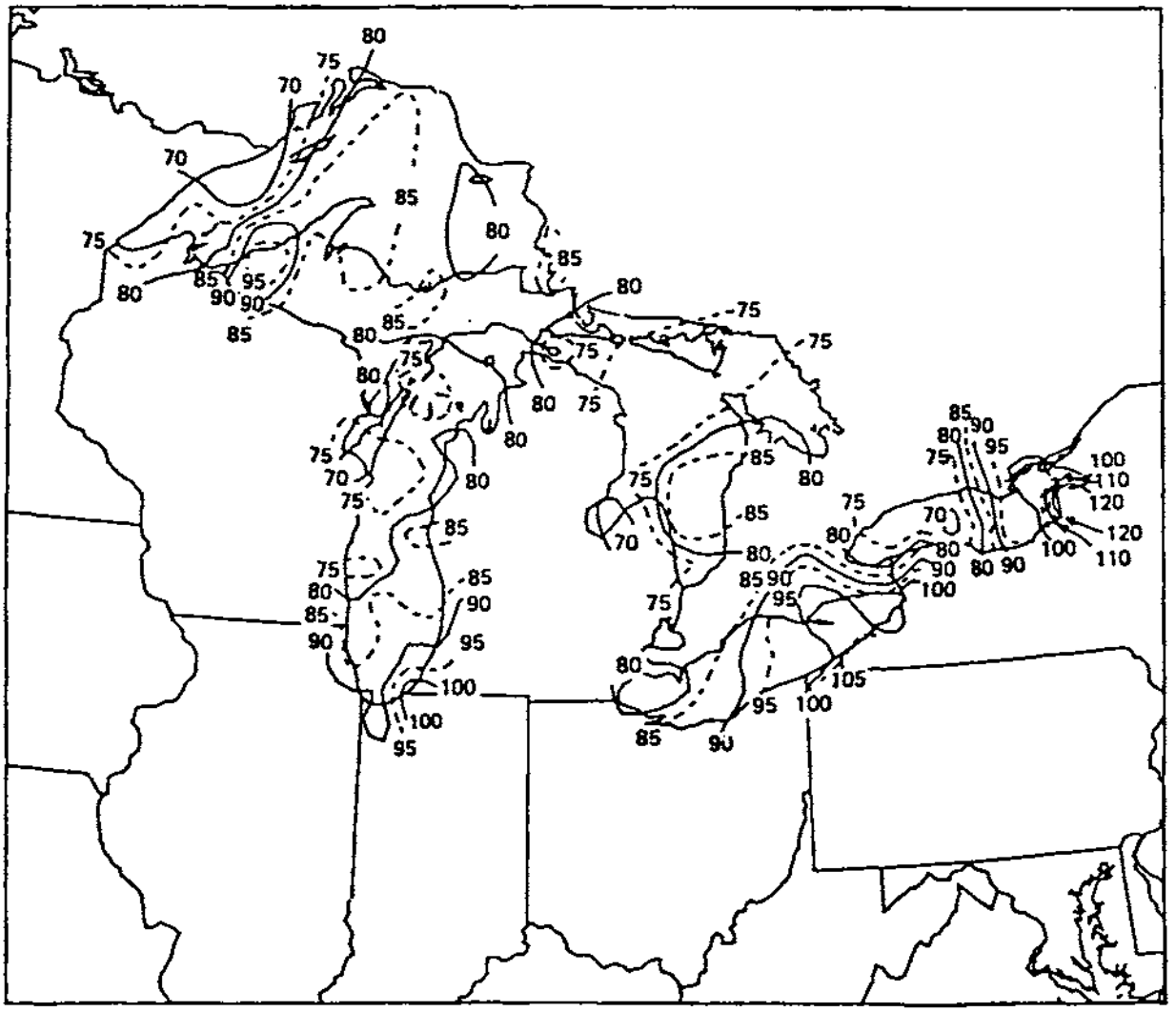

FIG. 4. Distribution of 30-year mean annual precipitation (cm) over the Great Lakes. Data source: National Climatic Center, Asheville, North Carolina.

ing loadings from the objective analysis method by amounts ranging from 17% for Lake Superior to 110% for Lake Ontario. For Pb (Table 2, Fig. 8), the upper limit wet-only loadings exceed those computed by objective analysis by percentages ranging from 13% for Lake Erie to 65% for Lake Superior.

The loadings estimates for wet-only deposition, based on GLAD data, are mostly smaller, and in some cases *much* smaller, than previous estimates of total atmospheric inputs based on *bulk* precipitation measurements. This is especially true for Cd (Fig. 7), for which loadings based on bulk measurements exceed even the upper-limit wet-only estimates by factors of 3.9, 7.9, 11.5, and 2.2 in Lakes Superior, Huron, Erie, and Ontario, respectively. For Pb (Fig. 8) the corresponding ratios are 2.3,3.0, 13.8, and 1.4, with a value of 1.8 for Lake Michigan as well.

Note that the total atmospheric loadings estimates for Lake Michigan (based on bulk measurements) are considerably smaller than those of most of the other lakes. These are based largely on bulk precipitation measurements made independently (Eisenreich 1980) of those of the rest of the Great Lakes (IJC 1977).

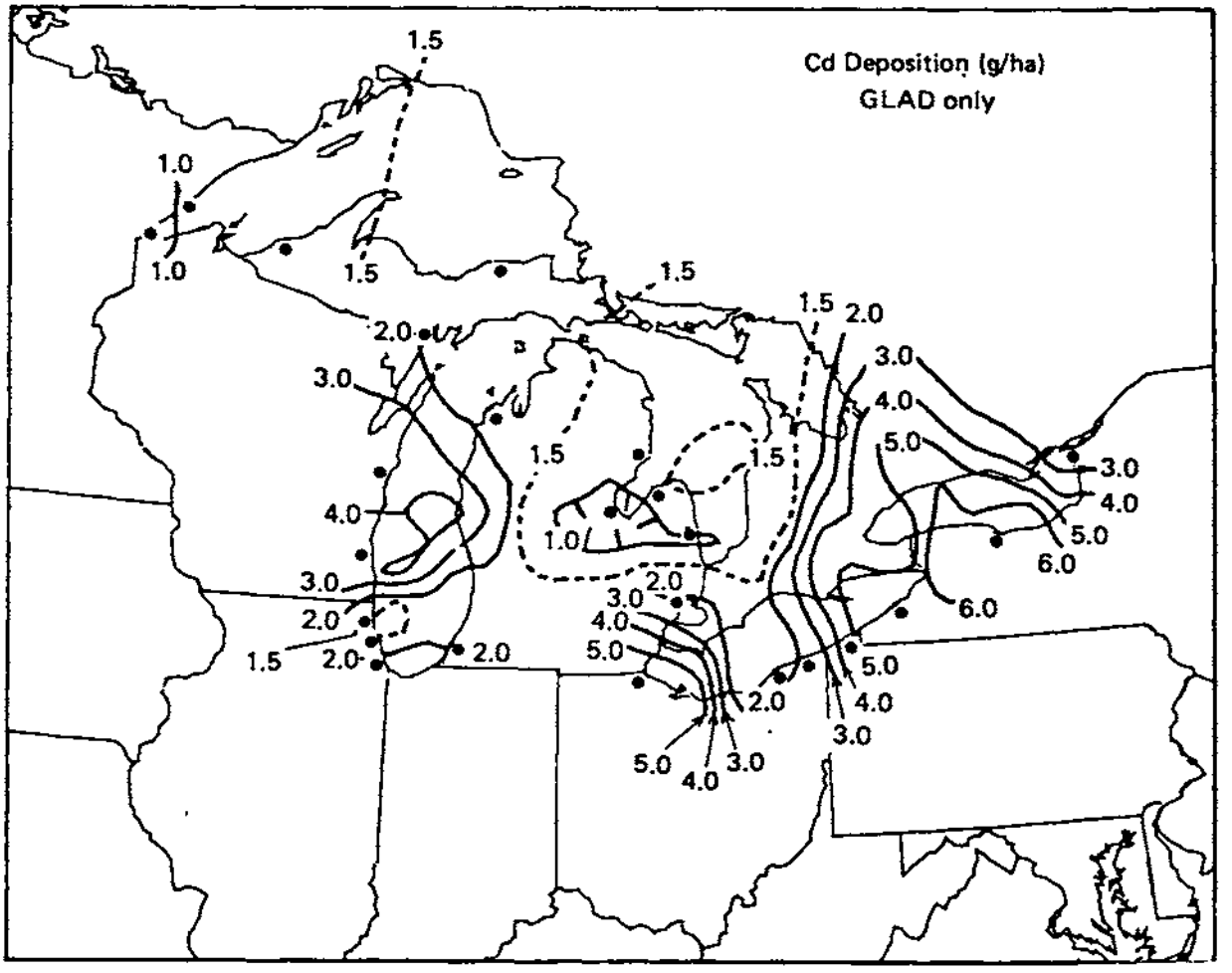

FIG. 5. Spatial distribution of annual deposition fluxes of Cd over the Great Lakes, using GLAD data, 1983. Solid circles are sampling stations that met the data completeness criteria and were used in this analysis.

If the current wet-only loadings accurately represent the wet-only loadings of the 1970s, and if bulk sampling gives a proper measure of total deposition, comparison of the GLAD objective analysis results to those of the bulk sampling implies that dry deposition accounted for 79-94% of the total atmospheric deposition of Cd to Lakes Superior, Huron, Erie, and Ontario. For Pb the same values for all five lakes range from 55% for Lake Ontario to 94% for Lake Erie.

For Cd (Fig. 7, Table 2) the loadings derived objectively from the GLAD wet-only data are mostly larger than both the wet and total deposition estimates from mass-balance modeling (Strachan and Eisenreich 1987). The ratios of GLAD objective wet-only loadings estimates to the wet deposition loadings estimates from mass-balance modeling are greater than 1 for four of the five lakes, and range from 0.91 for Lake Huron to 2.71 for Lake Ontario.

For Pb (Fig. 8, Table 2), however, the wet deposition loadings from the GLAD objective wet-only estimates were *lower* than those estimated by mass-balance modeling for all five lakes. The corresponding GLAD/modeling ratios range from 0.52 for Lake Michigan to 0.91 for Lake Superior. For two lakes (Superior and Ontario) the GLAD upper limit values are somewhat larger than the modeling values, however.

Finally, wet-only loadings estimates from this

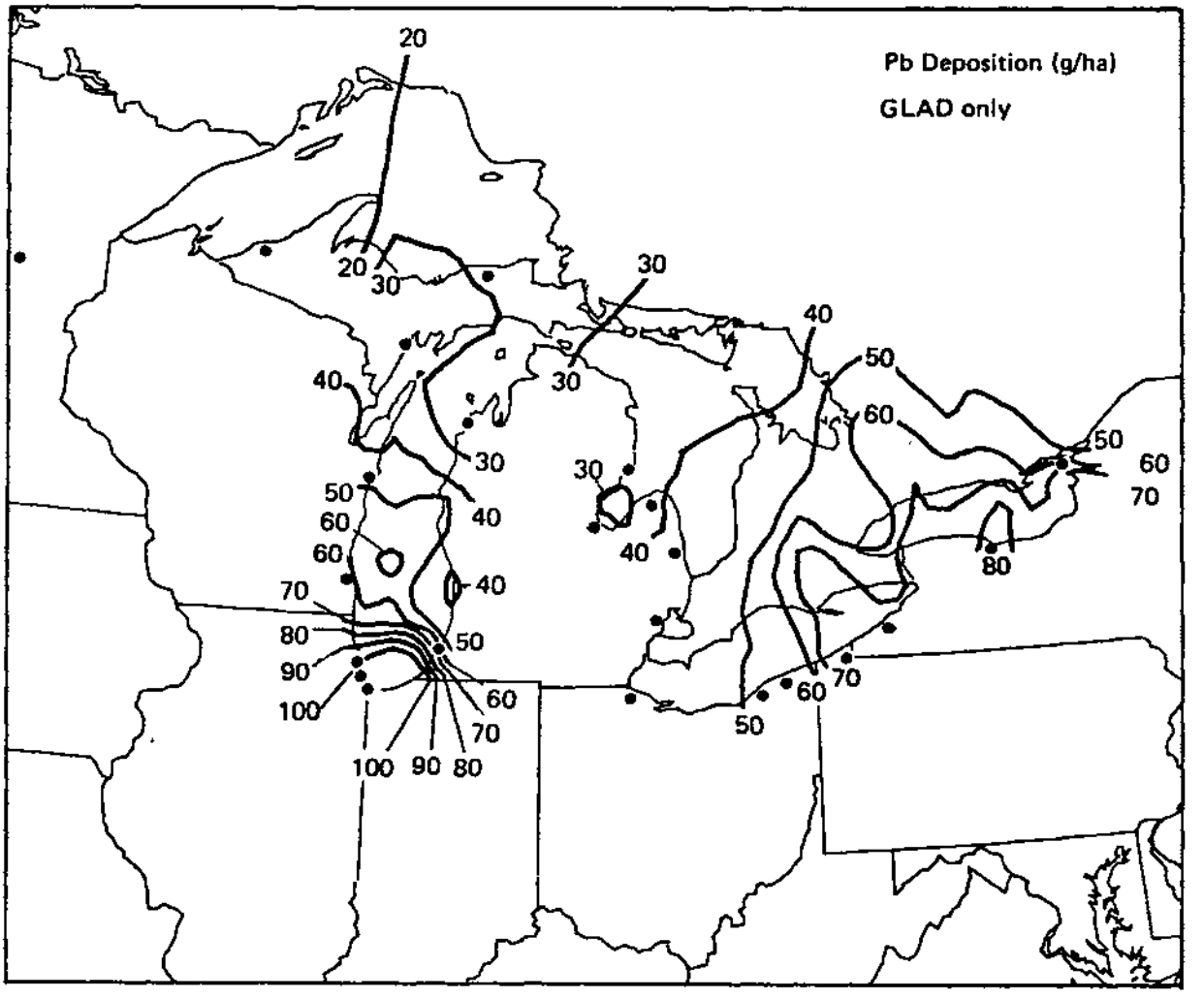

FIG. 6. Spatial distribution of annual deposition fluxes of Pb over the Great Lakes, using GLAD data, 1983. Solid circles are sampling stations that met the data completeness criteria and were used in this analysis.

study, presented in Table 2, are further summarized and compared in Table 3 with previous estimates of loadings from bulk sampling. Ratios of bulk precipitation loading to (upper limit) wet-only loadings are given for each element and each lake, based on data in Table 2. The results are summarized in the right hand column of Table 3, with a listing of the number of lakes having ratios of 3.0 or more for each element. A ratio of 3.0 corresponds to 67% of total atmospheric deposition occurring as dryfall. Note that the bulk/wet ratios for Cd and Pb are generally quite similar to those of Ca, Mg, K, and Na, in that for the most part, 2-4 lakes had values of 3.0 or more. The results for N and SO_4 are distinctly different, in that no lakes had ratios of 3.0 or more for either species.

These results are not explained simply as increased dry deposition associated with larger particles. Note that the ratios of Cd and Pb, which are typically found on particles having a mass median diameter smaller than 1 μm (Milford and Davidson 1985), are similar to those of the cations, for which mass median diameters are typically greater than 3 μm (Milford and Davidson 1985).

TABLE 2. Great Lakes wet-only loadings estimates, based on 1983 GLAD data (for Cd and Pb) and on GLAD and NADP data for 1982-83 (for all other ions), compared with related estimates in the literature.

Lake/method/component		Annual lake loadings							
		Cd tonnes	Pb tonnes	Ca Ktonnes	Mg Ktonnes	K Ktonnes	Na Ktonnes	N Ktonnes	SO_4 Ktonnes
Superior	GLAD wet-only								
	Objective analysis	12	170	19	3.4	3.1	3.5	36	104
	Est'd upper limit	14	281	22	4.0	4.4	3.8	48	131
	Mass balance model*								
	Wet	6.2	187						
	Dry	2.4	47						
	Total	8.6	234						
	Bulk sampling**	55	650	33	5.6	13	15	56	220
Michigan	GLAD wet-only								
	Objective analysis	15	240	17	3.3	2.8	3.4	37.6	118
	Est'd upper limit	20	354	21	4.3	4.0	6.6	42.0	133
	Mass balance model*								
	Wet	9.1	457						
	Dry	0.8	83						
	Total	9.9	540						
	Bulk sampling**	11	640	103	22	9.6	16	N/A	135
Huron	GLAD wet-only								
	Objective analysis	8.3	214	14	2.6	2.7	2.4	35	116
	Est'd upper limit	10.0	256	18	3.3	4.2	3.1	40	132
	Mass balance model*								
	Wet	9.1	318						
	Dry	0.9	86						
	Total	10.0	404						
	Bulk sampling**	79	780	280	8.2	32	45	52	230
Erie	GLAD wet-only								
	Objective analysis	8.7	142	12	2.2	2.2	3.3	19	90
	Est'd upper limit	13	160	14	2.5	3.2	4.0	21	100
	Mass balance model*								
	Wet	4.3	173						
	Dry	0.4	52						
	Total	4.7	225						
	Bulk sampling**	150	2,200	23	6.6	22	13	19	120
Ontario	GLAD wet-only								
	Objective analysis	9.5	125	5.1	1.0	1.1	1.5	15	61
	Est'd upper limit	20	201	7.4	1.4	1.5	1.6	17	79
	Mass balance model*								
	Wet	3.5	174						
	Dry	0.3	42						
	Total	3.8	216						
	Bulk sampling**	45	280	32	4.1	3.3	19	21	88

•Strachan and Eisenreich (1987)

•*Lake Michigan Eisenreich *et al.* (1977); remaining lakes: IJC (1977).

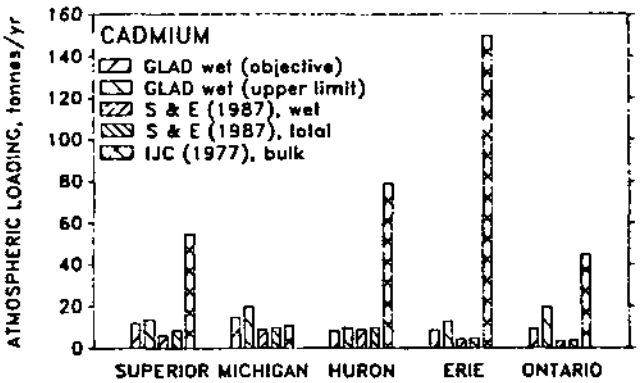

FIG. 7. Comparison of wet-only Cd loadings to the Great Lakes from GLAD data with previous estimates of wet-only and total atmospheric loadings.

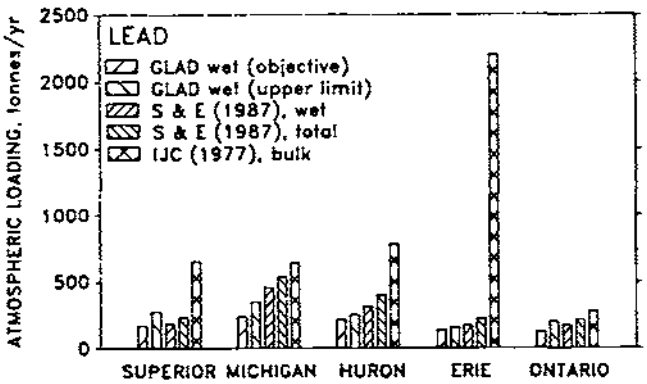

FIG. 8. Comparison of wet-only Pb loadings to the Great Lakes from GLAD data with previous estimates of wet-only and total atmospheric loadings.

DISCUSSION

There are several important results here:

1) For many elements the current wet-only loadings estimates are much smaller, for some of the lakes, than those made earlier based on bulk sampling, although these large differences are not seen for SO_4 and N.
2) Agreement between the current GLAD objective wet-only loadings estimates for Cd and Pb and the earlier wet-only loadings of Strachan and Eisenreich (1987) is much better. Still, the differences between their results and the GLAD results range from -63% (Lake Ontario) to + 10% (Lake Huron) for Cd and + 10% (Lake Superior) to +90% (Lake Michigan) for Pb, compared to the GLAD objective analysis results.

There are several possible ways to account for the differences between bulk and wet-only loadings estimates, and depending on the degree to which each contributes to the differences, there could be important implications regarding the direction of future research and policy for the Great Lakes. The differences may have been caused, at least in part, by one or more of the following:

1) Valid (i.e., uncontaminated, non-local) dry deposition to the bulk collectors,
2) Differences in the amount of precipitation implicit in the respective deposition estimates,
3) Reductions in airborne concentrations, caused bv reductions in Dollutant emissions.

TABLE 3. Comparison of current (upper limit) estimates of wet-only lake loadings with previous estimates based on bulk sampling

Species	Bulk loading/wet-only loading					Number >3.0
	Superior	Michigan	Huron	Erie	Ontario	
Cd	3.9	0.6	7.9	11.5	2.2	3
Pb	2.3	1.8	3.0	13.8	1.4	2
Ca	1.5	4.9	15.6	1.6	4.3	3
Mg	1.4	5.1	2.5	2.6	2.9	1
K	3.0	2.4	7.6	6.9	2.2	3
Na	4.0	2.4	14.5	3.2	11.9	4
N	1.2	*	1.3	1.0	1.2	0
SO_4	1.7	1.0	1.7	1.3	1.1	0

*Bulk loading estimates not available

between the measurements of the 1970s and those of the 1980s.

4) Analytical bias, or loss or gain of ions from container walls,
5) Contributions to the bulk collections by foreign substances (bird droppings, etc.) and/or resuspended local surface dust,

The first explanation to consider is that the differences between loadings derived from the bulk collector measurements and the wet-only measurements simply represent true dry deposition to the lake surfaces, unaffected by contamination. For some elements and some lakes, this may be a reasonable approximation of the truth, even though the physical characteristics of the dry collector bucket in no way simulate the water surface of a large lake. Sievering *et al.* (1984) estimated dry deposition of Pb to the southern basin of Lake Michigan at 200-500 tonnes/year. A rough extrapolation of these figures to the whole lake might give a range of 300-800 tonnes/year, which encompasses the observed 400 tonnes/year difference between recent (objective) wet-only loadings and the earlier bulk loadings. However, the mass balance modeling method of Strachan and Eisenreich (1987) (Table 2) gave a much lower value of 83 tonnes/year for the dry deposition loading of Pb to Lake Michigan.

For Cd in Lake Huron, and Cd and Pb in Lake Erie, as well as some of the alkaline ions in some of the lakes, if the entire difference between bulk and wet-only loadings was caused by valid dry deposition, then dry deposition is much more important in certain cases than has been thought up to now.

Differences in the annual precipitation amounts used to compute loadings from the respective bulk and wet-only concentration measurements are another possible reason for the observed differences in lake loadings. The bulk network was in operation during 1973 and 1974 (IJC, 1977), and loadings calculations were based on measured precipitation during the period of operation. In contrast, the observed (weighted mean) wet-only concentrations were converted to lake loadings using the 30-year mean annual precipitation for each lake, as described earlier. If actual precipitation during the bulk network operation was larger than the 30-year means, this would cause the loadings estimated from the bulk sampling data to be higher than those from the wet-only data, even if the concentrations were identical.

To evaluate this potential effect, annual direct inputs of precipitation to each of the five lakes for 1973 and 1974 were computed from precipitation data supplied by H. Hartmann (Personal communication, 1986). The largest departure from the 30-year mean for any lake in either year was + 6.0% for Lake Michigan in 1973. Thus, this difference in methods of estimating lake loadings cannot account for the observed large (factor of 2 and greater) differences in loadings.

Another possible reason for large differences between the loadings derived from the bulk measurements of the early 1970s and the wet-only measurements of the early 1980s is a reduction in airborne concentrations, caused by a reduction in emissions during the decade between the respective measurements. The USEPA reported (1985b) that Pb concentrations in air decreased by an average of 79% in 53 U.S. cities between 1976 and 1985, because of reductions in the Pb content of gasoline. Eisenreich *et al.* (1986) have noted an 82% reduction of the Pb flux in precipitation in Minneapolis and a similar 77% reduction in north-central Minnesota between 1979 and 1983. These reductions were closely related to the reduction in Pb used in gasoline in Minnesota.

No similar reduction in a major Cd source is known, but gradual reductions in Cd emissions may also have occurred between the mid-1970s and the early 1980s due to economic factors and gradual implementation of improved emission controls. However, similar reductions in emissions would not be expected for the terrestrially derived alkaline elements, which also exhibited large differences in loadings derived from the two sets of measurements. Thus, additional reasons for these differences must exist.

Analytical bias, or the loss or gain of ions from container walls, could possibly help to explain the differences. However, to resolve the differences, they must explain why results for the bulk samples are too high, or those for the wet-only samples are too low.

Since several laboratories analyzed samples from the bulk network (IJC 1977) and more than a decade later an entirely different laboratory analyzed samples from the GLAD wet-only network, analytical bias is a possible explanation for differences. Indeed, analytical difficulties caused bulk measurement sites with anomalously high analytical results to be excluded before lake loadings were estimated (IJC 1977). Without a direct comparison of laboratory performance on standard samples or split samples, analytical bias is difficult to assess.

In any case, analytical bias is not likely to be large enough to explain the observed differences of factors of two or more.

A related possible problem is the desorption or adsorption of metal ions from or by container walls. For desorption to have caused the observed differences, it would had to have affected the bulk collections. This is unlikely, because the bulk collector bags were acid-washed before use, and procedures for collection and analysis of blanks were adequate to have detected errors of the magnitude necessary to explain factor of two differences. Further, analyses of deionized distilled water stored in a bulk sample container for 1 month indicated no desorption of Cd or Pb from the container (Kramer 1973).

For adsorption on walls to have caused the observed differences, losses would had to have occurred in the polyethylene bags or bottles used respectively to collect and ship the GLAD samples, while occurring less, or not at all, in the earlier bulk samples.

The literature contains widely varying results of experiments to determine wall losses of metals from aqueous solution. For example, Chan *et al.,* (1983) have reported minimal losses of Pb to polyethylene bags from synthetic and actual precipitation samples for contact periods as long as 29 days at room temperature. On the other hand, from solutions of metal salts in acidified (pH 4.5) deionized water at room temperature, Good and Schroder (1984) observed losses of Pb as high as 96% to polyethylene over 17 days.

A potentially crucial feature of wall-loss experiments — the presence or absence of natural rain-borne suspended solids — was emphasized by Rattonetti (1976). He found that the loss of Pb ions to container walls over 10-12 days was insignificant compared with adsorption of the metal ions by the solid particles present in natural precipitation samples. In the GLAD network ions adsorbed on particles in the samples would be desorbed by acidification of the unfiltered sample, and should have been properly detected during analysis.

A similar situation prevails for Cd, although the literature is in better agreement than for Pb. Chan *et al.* (1983) observed about a 10% loss of Cd over 29 days at room temperature. Shendrikar *et al.* (1984) reported approximately 20% losses of Cd from double distilled water acidified to a pH of less than 2 to polyethylene within about 10 days of storage time at 25°C, but no further losses at longer storage times. Rattonetti (1976) also reported insignificant losses of Cd to container wall, compared with adsorption to suspended solids in precipitation samples.

Thus the literature strongly indicates that a 10-20% loss of Cd by adsorption on container walls should be an upper limit during the sampling periods of a week or more used in the GLAD network. Such losses can be reversed if the samples are allowed to remain in contact with the collector or container for 6-24 hours following the addition of acids (Tramontano *et al.* 1987). Such a loss and subsequent recovery were observed in the bulk network (Kramer 1973), but in the GLAD network acids were not added until the samples had been removed from the sampler, shipped to the laboratory in a separate container, and then split and placed in another polyethylene sample bottle.

Thus, contamination of the bulk samples by desorption from container surfaces is not a likely cause of the observed differences between the bulk and wet-only samples. Unrecovered losses of Cd to sampler or container walls (perhaps 10-20%) could have occurred in the GLAD samples, but are not large enough to explain the large differences between estimates of lake loadings derived from bulk and wet-only sampling.

If interactions between precipitation samples and collector or container walls cannot explain the observed differences, we must look for other possible reasons why the bulk samples would have contained more metals and other ions.

One such explanation is that the bulk sampler collections included sizeable contributions from resuspended local surface dust. This dust would include wind-blown emissions from soils and emissions caused by vehicle traffic on both paved and unpaved roads. Thus, it would naturally contain the major base cations, and at times also Na and Cl from winter road salting. In urban and industrial locations, it might well also contain high concentrations of Pb, Cd, and other pollutant metals, which are known to occur in high abundance sorbed on surface dust after previous wet or dry deposition (Hopke *et al.* 1980, Harrison *et al.* 1981). On the other hand, any previously deposited *soluble* anions (e.g., SO_4 and N) in surface dust would be leached into deeper soil layers by subsequent rainfall, so contamination of bulk samplers by resuspended local surface dust would not cause significant differences between bulk and wet-only collections for SO_4 and N. This explanation is con-

sistent with the small differences between bulk and wet-only loadings for these ions shown in Table 3.

It is not surprising that open samplers would be vulnerable to contamination from local resuspended dust. Stensland and Semonin (1984) pointed out that, even in samplers that open and close automatically, poor lid-to-bucket seals can result in samples being contaminated by fugitive dust.

If the observed differences between Cd and Pb loadings derived from bulk measurements and those derived from wet-only measurements are caused by contamination of the bulk samplers by resuspended surface dust, such contamination should occur preferentially in urban and industrial locations, where the surface dust most likely would be contaminated with these metals. This suggests that ratios of Cd and Pb loadings from bulk sample measurements to those from wet-only measurements would be greater in urban locations than rural locations. A test of this hypothesis is possible from the measurements of Sanderson *et al.* (1985). This group measured atmospheric loadings of Cd and Pb, using bulk and wet-only measurements at urban and rural locations in and near Windsor, Ontario. For Pb the ratio of the loadings derived from the bulk measurements to those from the wet-only measurements was 2.61 at an urban site and 1.33 at a rural site. For Cd the respective ratios were 1.8 and 1.4. These results are in qualitative agreement with the hypothesis outlined above, but the relatively small differences in ratios between the urban and rural locations do not appear to be large enough to explain the differences between loadings derived from bulk and wet-only measurements in Figures 7 and 8.

Similar comparisons of bulk and wet-only collections of filtered (0.4 /on) particulate matter at urban (Milwaukee) and rural (Kewaunee, Wisconsin) sites on Lake Michigan, for 8 months during 1976, were reported by Eisenreich *et al.* (1977). The bulk/wet-only ratios of the volume-weighted mean total particle concentrations were 15.9 at the urban site and 3.9 at the rural site. Since urban surface dust is likely to be more contaminated with Pb and other metals than dust resuspended in rural areas, a similar or greater difference in bulk/wet-only deposition of Pb would be expected for these two sites. Thus, these data support the hypothesis that contamination of urban bulk samplers by resuspended local surface dust is a major reason for the observed differences between loadings estimated from the recent wet-only measurements and those derived from previous bulk measurements.

Some would argue that deposits of local resuspended dust *should* be included when tallying atmospheric deposition inputs to the lakes. There are several reasons why this would be risky. It is true, of course, that some surface dust resuspended over land areas will travel over, and fall into the lakes, but the affected areas of the lakes are not known with any accuracy. The flux of locally resuspended dust to the lakes would be greatest at the shoreline and decrease as some unknown function of distance away from shore. The second reason is the absence of a proven method for estimating the "locally resuspended" portion of the deposition measured in bulk samples. A third reason is the lack of procedure to estimate deposition to a water surface, or any other natural surface, from that measured in a bulk collector.

If indeed local surface dust accounts for much of the difference between the lake loadings estimated from bulk and wet-only collections, then it is likely that loadings derived from bulk measurements overestimate the contribution of atmospheric deposition to the total input of Pb and Cd.

An interesting parallel exists between 1) the observation noted in this paper that recent observations of wet-only metal loadings to the Great Lakes are much lower than those measured previously in bulk precipitation in the middle-1970s, and 2) similar differences between recent and earlier *wet-only* measurements noted by Barrie *et al.* (1987) and Tramontano *et al.* (1987). Both Barrie *et al.* and Tramontano *et al.* ascribe the differences they noted to contamination and artifacts present in the earlier data. Since the GLAD data appear to avoid contamination by resuspended local surface dust, but are not quite as rigorous with respect to certain procedures (e.g., acid-washing of sample containers before use, and desorption of metals from container walls afterwards) as the methods currently recommended (Tramontano *et al.* 1987), the Great Lakes loadings derived from the GLAD data still have some fundamental uncertainties associated with them. They may still be upper limits of the true precipitation loadings, owing to certain possible contamination allowed by present procedures. On the other hand, if wall losses are the dominant bias, it appears current loadings estimates cannot be more than about 20% less than the true wet-only loadings.

Compared to the large differences between the

GLAD objective wet-only loadings and those derived from the bulk measurements of the 1970s, the differences between the GLAD and the mass-balance wet-only loadings are small (Table 2, Figs. 7 and 8). Still, many of the differences are more than 50% of the GLAD loadings. For Cd, the wet-only loadings estimated from the GLAD data exceed those of Strachan and Eisenreich (1987) for all of the lakes except Huron. The difference is greatest for Lake Ontario, where the mass balance estimate is only 37% of the GLAD objective analysis result, the least for Lake Huron, where the mass balance result is higher by 10%.

For Pb, the differences are in the opposite direction. The mass-balance wet-only loading is higher for all five lakes. The smallest difference exists for Lake Superior, where the mass-balance result is 10% higher than that of the GLAD objective analysis. The largest difference is for Lake Michigan, where the mass-balance result is 90% higher.

The dry deposition loadings estimates of Strachan and Eisenreich (1987) (listed specifically in Table 2, and indicated in Figs. 7 and 8 as the differences between total and wet-only mass balance estimates) may be compared with those made by assuming that bulk collections less wet-only collections (Figs. 7 and 8) equal dry deposition. For Cd, the dry loadings to the Great Lakes calculated by Strachan and Eisenreich range from 0.3 to 2.4 tonnes/year (Table 2), while the dry loadings obtained by subtracting the *maximum* wet-only loading (including the estimated upper limit for the GLAD data) from the bulk loadings range from 25 to 41 tonnes/year (excluding Lake Michigan, where the difference is negative). For Pb, the dry loadings of Strachan and Eisenreich range from 42-86 tonnes/year, while those derived by subtraction of the maximum wet loadings estimate from the bulk loadings range from 79-2,027 tonnes/year. Even without making a detailed lake-by-lake comparsion, the large differences in dry loadings obtained by these two methods are evident, and suggest the possibility of contamination of the bulk samples must be examined.

Only a few estimates of dry deposition of metals to the Great Lakes exist. Although such measurements are badly needed to understand this route of atmospheric deposition to the lakes, the methods currently available are inadequate, and further research is needed to develop adequate methods.

SUMMARY AND CONCLUSIONS

Loadings of Cd, Pb, and other ions to the Great Lakes from precipitation alone are estimated from GLAD network measurements of precipitation composition on the lakes. For most ions, these loadings are considerably smaller than those measured in the early 1970s using bulk precipitation samples.

For Cd, Pb, and the alkaline ions, the ratios of loadings derived from bulk measurements to those from wet-only measurements for the individual lakes frequently exceeded 3. For Pb, some portion of these differences can be accounted for by a reduction in emissions caused by the reduction in the Pb content of gasoline. For Cd and Pb, losses to the wet collector walls may account for a small portion of the differences.

For all species, dry deposition to the open bulk collectors accounts for some of the differences. For sulfate and the nitrogen compounds, for which the ratio of bulk to wet-only loadings exceeded 2 only once, dry deposition can account for most or all of the differences.

For the most extreme differences between the bulk and wet-only loadings, contamination of the bulk collectors by local resuspended surface dust is likely to be a major cause.

The wet-only loadings derived from the GLAD measurements agree mostly within a factor of two with those of Strachan and Eisenreich (1987), based on mass-balance calculations. The relatively close agreement of these two studies indicates that Great Lakes water quality policies and planning based on the loadings derived from the earlier bulk sampling should be reexamined with the understanding that atmospheric contributions are likely to be considerably smaller than previously estimated.

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REFERENCES

Achtemeier, G. L. 1987. On the concept of varying influence radii for a successive corrections objective analysis. *Monthly Weather Review* 115:1760-1771.

_____, Hildebrand, P. H., Schickedanz, P. T., Ackerman, B., Changnon, S. A., and Semonin, R. G. 1977. *Illinois Precipitation Enhancement Program and Evaluation Techniques for the High Plains Cooperative Program.* Final Report, Contract 14-06-D-7191. Illinois State Water Survey, Champaign, 6-12, Appendix B.

Acres Consulting Services, Ltd. 1975. Atmospheric loading of the upper Great Lakes, Volume 2, Main Text, Report to Canada Centre for Inland Waters, Acres Consulting Services, Ltd., Niagara Falls, Ontario, Table 4.5.

_____. 1977. Atmospheric loading of the lower Great Lakes and the Great Lakes drainage basin, Report to Canada Centre for Inland Waters, Acres Consulting Services, Ltd., Niagara Falls, Ontario, p. 43.

Allen, H. E., and Halley, M. A. 1980. Assessment of airborne inorganic contaminants in the Great Lakes. Appendix B of the Great Lakes Science Advisory Board 1980 Annual Report to the International Joint Commission. International Joint Commission, Washington, D.C.

Barnes, S. L. 1964. A technique for maximizing details in numerical weather map analysis. *J. Appl. Meteorol.* 3:396-409.

_____1973: *Mesoscale objective map analysis using weighted time-series observations.* NOAA Tech. Memo. ERL NSSI-62. [NTIS COM-73-10781].

Barrie, L. A., Lindberg, S. E., Chan, W. H., Ross, H. B., Arimoto, R., and Church, T. M. 1987. On the concentration of trace metals in precipitation. *Atmos. Environ.* 21:1133-1135.

Chan, C. H., and Kuntz, K. W. 1982. Lake Ontario atmopsheric deposition, 1969-1978. *Wat., Air, Soil Pollut.* 18:83-99.

Chan, W. H., Tomassini, F., and Loescher, B. 1983. An evaluation of sorption properties of precipitation constituents on polyethylene surfaces. *Atmos. Environ.* 17:1779-1785.

De Pinto, J. V., Young, T. C, and McIlroy, L. M. 1986. Great Lakes water quality improvement. *Environ. Sci. Technol.* 20:752-759.

Eisenreich, S. J. 1980. Atmospheric input of trace metals to Lake Michigan. *Wat., Air, Soil Pollut.* 13:287-301.

_____1982. Atmospheric role in trace metal exchange at the air-water interface. *J. Great Lakes Res.* 8:243-256.

_____, Emmling, P. J., and Beeton, A. M. 1977. Atmospheric loading of phosphorous and other chemicals to Lake Michigan. *J. Great Lakes Res.* 3:291-304.

_____, Hollod, G. J., and Johnson, T. C. 1981. Atmospheric concentrations and deposition of polychlorinated biphenyls to Lake Superior. In *Atmospheric Pollutants in Natural Waters,* ed. S. J. Eisenreich, pp. 425-444. Ann Arbor, Michigan: Ann Arbor Science Publishers.

_____, Metzer, N. A., and Urban, N. R. and Robbins, J. A. 1986. Response of atmospheric lead to decreased use of lead in gasoline. *Environ. Sci. Technol.* 20:171-174.

Gatz, D. F. 1975: Pollutant aerosol deposition into southern Lake Michigan. *Wat., Air, Soil Pollut.* 5:239-251.

_____, Bowersox, V. C, and Su, J. 1987. *Great Lakes Atmospheric Deposition (GLAD) network, 1982-1983: data analysis and interpretation.* Final Report, Contract R005882-01, USEPA Great Lakes National Program Office, Illinois State Water Survey. Champaign 61280.

Good, A. B., and Schroder, L. J. 1984. Evaluation of metal ion absorptive characteristics of three types of plastic sample bags used for precipitation sampling. *J. Environ. Sci. Health* A19(5):631-640.

Great Lakes Water Quality Board. 1985.*1985 report on Great Lakes water quality.* Report to the International Joint Commission, Kingston, Ontario, June, 1985. Available from the IJC, Great Lakes Regional Office, P.O. Box 32869, Detroit, MI 48232-2869.

Harrison, R. M., Laxen, D. P. H., and Wilson, S. J. 1981. Chemical associations of lead, cadmium, copper, and zinc in street dusts and roadside soils. *Environ. Sci. Technol.* 15:1378-1383.

Hicks, B. B., Wesely, M. L., and Durham, J. L. 1980. *Critique of methods to measure dry deposition.* Workshop Summary, USEPA Report No. EPA-600/9-80-050, NTIS PB81-126443.

Hopke, P. K., Lamb, R. E, and Natusch, D. F. S. 1980. Multielemental characterization of urban roadway dust. *Environ. Sci. Technol.* 14:164-172.

International Joint Commission. 1977. *Atmospheric loading of the lower Great Lakes and the Great Lakes drainage basin.* Report, International Reference Group on Great Lakes Pollution from Land Use Activities. Available from IJC, 100 Ouellette Ave., Windsor, Ontario N9A 6T3.

Kramer, J. R. 1973. *Fate of atmospheric sulphur dioxide and related substances as indicated by chemistry of precipitation.* Report to the Ontario Ministry of the Environment. Dept. of Geology, McMaster University, Hamilton, Ontario, Canada.

Milford, J. B., and Davidson, C. I. 1985: The sizes of particulate trace elements in the atmosphere — a review. *J. Air Pollut. Control Assoc.* 35:1249-1260.

Murphy, T. J., Schinsky, A., Paolucci, G., and Rzeszutko, C. P. 1981. Inputs of polychlorinated biphenyls to Lakes Huron and Michigan. In *Atmospheric Pollutants in Natural Waters,* ed. S. J. Eisenreich, pp. 445-458. Ann Arbor, Michigan: Ann Arbor Science Publishers.

National Climatic Center. 1982. Monthly Normals of Temperature, Precipitation, and Heating and Cooling Degree Days. In *Climatography of the United States, No. 81,* National Climatic Center, NOAA, Asheville, NC.

Rattonetti, A. 1976: Stability of metal ions in aqueous environmental samples. In *Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis.* Proceedings of the 7th IMR Symposium, pp. 633-648. National Bureau of Standards Special Publication 422.

Rice, C. P., Samson, P. J., and Noguchi, G. E. 1986. Atmospheric transport of toxaphene to Lake Michigan. *Environ. Sci. Technol.* 20:1109-1116.

Rodgers, P. W., and Swain, W. R. 1983. Analysis of polychlorinated biphenyl (PCB) loading trends in Lake Michigan. *J. Great Lakes Res.* 9:548-558.

Sanderson, M., Marchand, D., and McQuarrie, P. 1985. Surface deposition of lead and cadmium from the atmosphere in the Detroit River – Lake St. Clair region. *J. Great Lakes Res.* 11:305-312.

Schmidt, J. A., and Andren, A. W. 1984. Deposition of airborne metals into the Great Lakes: an evaluation of past and present estimates. In *Toxic Contaminants in the Great Lakes,* ed. J. O. Nriagu and M. S. Simmons, pp. 81-103. Vol. 14, Advances in Environmental Science and Technology Series. New York: John Wiley.

Shendrikar, A. D., Filby, R., Markowski, G. R., and Ensor, D. S. 1984. Trace element loss into polyethylene container walls from impinger solutions from flue gas sampling. *J. Air Poll. Control Assoc.* 31:233-236.

Sievering, H., Dolske, D. A., Jensen, V., and Hughes, R. L. 1984. *An experimental study of lake loading by aerosol transport and dry deposition in the Lake Erie Basin.* Report EPA-905/2-84-002, USEPA Great Lakes National Program Office, Chicago, Illinois.

Stensland, G. J., and Semonin, R. G. 1984. Response. *Bull. Amer. Meteorol. Soc.* 65:640-643.

Strachan, W. M. J., and Eisenreich, S. J. 1987. *Mass balancing of toxic chemicals in the Great Lakes: the role of atmospheric deposition.* Report of the Workshop on the Estimation of Atmospheric Loadings of Toxic Chemicals to the Great Lakes Basin, Scarborough, Ontario, 29-31 October 1986.

Todd, D. K., ed. 1970. *The Water Encyclopedia.* Port Washington, New York: Water Information Center, p. 127.

Tramontano, J. M., Scudlark, J. R., and Church, T. M. 1987. A method for the collection, handling, and analysis of trace metals in precipitation. *Environ. Sci. Technol.* 21:749-753.

USEPA. 1985a. Five year program strategy for Great Lakes National Program Office, 1986-1990. USEPA, Great Lakes National Program Office, Chicago, EPA-905/9-85-002.

_____. 1985b: National air quality and emissions trends report. USEPA Report NO. 450/4-87-001.

_____. (undated-a). Standard operating procedure for sample analysis and data reporting, atmospheric monitoring program. EPA Contract #68-04-5038, Task 5; inorganic parameters. (Working Draft) USEPA, Great Lakes National Program Office, Chicago, Illinois.

_____. (undated-b). Atmospheric deposition and precipitation sampling network station operator's manual USEPA, Great Lakes National Program Office, Chicago, Illinois.

Whitehead, H. C, and Feth, J. H. 1964. Chemical composition of rain, dry fallout, and bulk precipitation at Menlo Park, California, 1957-1959. *J. Geophys. Res.* 69:3319-3333.

Winchester, J. W., and Nifong, G. 1971. Water pollution in Lake Michigan by trace elements from pollution aerosol fallout. *Wat., Air., Soil. Pollut.* 1:50-64.